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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

A METHOD FOR THE MICROPHOTOMETRIC TITRATION OF MATERIAL IN ULTRAVIOLET LIGHT IN WHICH THE END POINT IS RECORDED

COMMUNICATION I. THE DESIGN OF A MICROTITRATOR AND THE DETERMINATION OF IRON CONTENT

K. P. Stolyarov, N. N. Grigor'ev, and Ch'en Kuo-Liang

A.A. Zhdanov Leningrad State University

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Recently, microchemical methods for the quantitative determination of materials (particularly titrimetric methods) have found wide application. The main disadvantage of microtitrimetric determinations is the relatively large indicator error. A large number of titration methods which do not involve the use of indicators (amperometry, potentiometry, etc.) and which are based on the use of the usual type of apparatus, but with smaller absolute volumes of the test material, have been suggested in order to eliminate this indicator error. Nevertheless, the complexity of the apparatus and the large number of factors which affect the experimental results have hindered the wide application of these methods in microchemical practice.

Earlier [1], one of the authors of the present article suggested a visual method for the titration of materials without an indicator in ultraviolet light. The method is fairly simple and effective. The method can be widely used for microtitrimetric determination of materials with variable valence. In combination with various masking methods (e. g., complexonometric), and by using special organic reagents, this method can be used for the determination of elements with a constant valence (in precipitation and neutralization methods, and in others).

Normal microchemical methods permit, as a rule, the determination of the content of a component in very small amounts of test material, in those cases where the latter contains a high content of the component to be determined (sometimes up to 90-100%). The method suggested is applicable in those cases where the absolute content of the test component in microsamples amounts to a fraction of a percent. Under these conditions the relative error does not exceed 0.5-2.0%. There is no need to carry out complex calculations of the titration errors.

Microchemical photometric titration in ultraviolet light is carried out by means of a specially constructed microtitrator which ensures an objective recording of the end point.

Microtitrator design. The apparatus is shown schematically in Fig. 1. Light from an ultraviolet radiation source 1 (a PRK-4 tube) is split into two beams: the analytical and compensating beams. The analytical beam passes through a light filter 6, the cuvette with the material to be titrated 5, a variable slit 4, a luminescent screen 3, and a receiver for the radiation 2. The compensating beam passes through a light filter 6', a variable slit 4', and a receiver for the radiation 2'. The photocurrent is recorded by means of a mirror galvanometer 7, which is connected through a resistance 8 and a shunt resistance 9. The light filter 6 used is a Mark UFS-3 light filter, whose transmission curve is shown in Fig. 2. The titration cuvette is a vessel with plane parallel sides and with capacity of 3-4 ml; it is made from ordinary optical glass, which readily passes ultraviolet radiation with a wavelength of 365 mμ. The slits 4 and 4' are designed for arbitrarily changing the value of the light beam. The

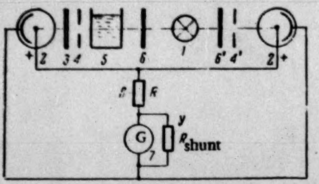

Fig. 1. Schematic diagram of the microtitrator. 1. Ultraviolet radiation source; 2,2') photoelements; 3) luminescent screen; 4,4') variable slits; 5) cuvette containing the material to be titrated; 6,6') light filters; 7) mirror galvanometer; 8) resistance; 9) shunt.

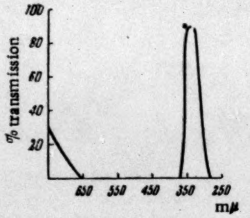

Fig. 2. Transmission curve of the UFS-3 light filter.

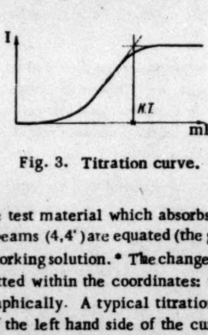

Fig. 3. Titration curve.

TABLE 1

Fe, mg			Fe, mg		
taken	found	absolute error	taken	found	absolute error
6.27	6.25	—0.02	3.58	3.60	+0.02
6.27	6.25	-0.02	2.23	2.25	+0.02
5.33	5.35	—0.03	2.23	2.22	-0.01
5.38	5.35	-0.03	1.15	1.13	-0.02
4.48	4.48	0	1.15	1.14	-0.01
4.48	4.46	-0.02	0.38	0.39	+0.01
3.58	3.57	—0.01	0.38	0.40	+0.02

TABLE 2

HCl conc., N	Fe, mg		
	taken	found	absolute error
0.2	2.87	2.89	+0.02
0.2	2.87	2.86	—0.01
0.4	2.23	2.25	+0.02
0.4	2.23	2.25	+0.02
0.8	2.87	2.86	—0.01
0.8	2.87	2.89	+0.02

radiation receivers are selenium photoelements with a maximum sensitivity at 580 mμ. Accordingly, in order to increase the sensitivity of the apparatus we introduced a luminescent screen 3 in order to convert the ultraviolet radiation into visible radiation; the screen was made from uranium glass or any other luminescent material. The light filter 6' is chosen so that its maximum transmission is near the maximum sensitivity of the photoelement.

The apparatus is connected into a compensation scheme, while the photoelements are irradiated from one light source; accordingly, when the parameters of the photoelements are correctly chosen there is no need for a particularly careful stabilization of the ultraviolet radiation source.

The test material which absorbs ultraviolet radiation is introduced into the cuvette. The intensities of the two light beams (4,4') are equated (the galvanometer reading should be zero), and titration carried out with known portions of working solution.* The changes of the photocurrent with the amount of reagent added are recorded, and a curve plotted within the coordinates: volume (in ml) of titrant – galvanometer reading. The end point is determined graphically. A typical titration curve is shown in Fig. 3. It is sufficient to obtain a few points on the linear section of the left hand side of the curve and a few points on the right hand side (where the galvanometer reading is constant). This enables the time taken to carry out a titration to be cut down appreciably without affecting the final results.

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*The working solution (titrant) is introduced into the cuvette containing the solution to be titrated by means of a microburet with a capacity of 2 ml and with scale divisions of 0.01 ml, the tip of the microburet being immersed in the solution; the microburet is provided with a pneumatic seal and a microscrew. The use of a similar type of buret, which has been described by us previously in [2], almost completely eliminates the drop error.

TABLE 3

Concentration	Fe, mg		
	taken	found	absolute error
0.8 $N\ H_2SO_4$	1.20	1.25	+0.05
0.4 $N\ H_2SO_4$	1.20	1.21	+0.01
0.6 $N\ HNO_3$	1.20	1.33	+0.13
0.6 $N\ HNO_3$	0.90	0.98	+0.08
0.6 $N\ HNO_3$	0.60	0.75	+0.15

TABLE 4

Fe taken, mg	Added, mg	Fe found, mg	absolute error, mg	Limiting ratio Fe : Me
	Co^{2+}			
2.23	29.45	2.24	+0.01	1 : 13
2.23	73.63	2.24	+0.01	1 : 33
2.23	117.90	2.25	+0.02	1 : 50
	Ni^{2+}			
2.87	5.86	2.87	0	1 : 2
2.87	88	2.90	+0,03	1 : 30
2.87	117.3	2.90	+0,03	1 : 40

TABLE 5

Sample wt., mg	Fe, mg		Fe content, %	
	added	found	found	specified content
0.4642	–	5.06	1.09	1.02
0.4776	–	4.86	1.02	1.02
0.4776	7.2	12.12	1.03	1.02

The technique used for determination of iron content. The method suggested for the iodometric microdetermination of iron is based on the well known reaction $2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$, the liberated iodine being titrated with sodium thiosulfate. The only component which absorbs in the working part of the spectrum (λ_{max} = = 365 mμ) in this case is elementary iodine. Divalent iron in hydrochloric acid solution has an absorption band with an origin at 300 mμ, while potassium iodide absorbs about 250-280 mμ and sodium thiosulfate and sodium dithionate are also transparent in the spectral region chosen.

The iron content is determined as follows. To 2-3 ml of the test solution, which is a hydrochloric acid solution of a trivalent iron salt and which is contained in the titration cuvette, is added excess potassium iodide; after a certain time interval, sufficient for the reaction to go to completion, the apparatus is brought to the operating state, and the tip of the microburet containing the sodium thiosulfate solution introduced into the cuvette; the titrant is then added, with constant stirring, until the galvanometer readings do not change appreciably on adding the titrant; a titration curve is then constructed and the iron content determined graphically.

Table 1 contains the results for the determination of iron in 1 N hydrochloric acid.

The results given in Table 2 show the relation between the experimental results and the acidity of the solution.

It is evident from Tables 1 and 2 that determination of iron content by this method gives completely satisfactory results.

Sulfuric, nitric, and hydrochloric acids are most frequently used for dissolving test material; accordingly, we thought it would be of interest to study the effect of sulfuric and nitric acids on the results of iron determination.

It is clear from Table 3 that nitric acid affects the results to the greatest extent; this is, presumably, related to its oxodizing capacity. Cobalt and nickel do not interfere with the iron determination (Table 4).

Arsenic and copper, which themselves oxidize iodide to the elementary state, interfere with the iodometric determination of iron; tin, lead antimony, bismuth, and mercury also interfere. We removed these elements from solution by cementation on metallic aluminum; removal of the elements indicated is quantitative. Such a technique enables iron to be determined in materials containing relatively large amounts of the elements indicated.

TABLE 6

Sample wt., g	Fe found, mg	Fe content, %	
		found	specified content
0.3150	2.33	0.74	0.76
0.2716	1.91	0.71	0.76

TABLE 7

Expt. No.	Fe found, %	
	by the suggested method	by the dichromate method
1	4.31	4.42
2	4.28	4.42

Determination of the iron content of bronze. An aliquot of the test sample is dissolved by heating in nitric acid, concentrated sulfuric acid is added to the solution obtained, and the solution evaporated until sulfuric acid fumes appear. The sulfates are dissolved in water and hydrochloric acid is added. Cementation is then carried out on an accurately weighed amount of aluminum metal (0.4 g). Copper and other elements are removed by filtration. The solution obtained is evaporated to a small volume, the nitric acid is oxidized, and precipitation effected with ammonium hydroxide. The precipitate is dissolved in 1 N hydrochloric acid and the solution transferred to a 25 ml standard flask, in which it is made up to the mark with 1 N hydrochloric acid; the iron is determined in an aliquot of this solution as described above. In parallel, experiments are carried out with the same amount of aluminum. The results obtained are given in Table 5.

Determination of the iron content of a manganese concentrate. An aliquot of the concentrate is decomposed with concentrated hydrochloric acid, the solution obtained is neutralized with ammonia, and then some more hydrochloric acid added to establish a definite acidity. The solution obtained is transferred to a 25 ml standard flask, and its volume made up to the mark with distilled water. The iron content is determined on an aliquot of this solution (Table 6).

Determination of the iron content of an ore. An aliquot of the ore is decomposed by heating with aqua regia, the solution is evaporated to a small volume and 3 ml of concentrated sulfuric acid added; the solution is again evaporated until sulfuric acid fumes appear. The residue is dissolved in water, and, after filtering the solution, precipitation carried out with ammonium hydroxide. The washed hydroxide precipitate is dissolved on the filter in 1 N hydrochloric acid, and the filtrate transferred to a 25 ml standard flask. The iron content is determined on an aliquot of the solution. For comparison, iron was also determined by the dichromate method (Table 7).

SUMMARY

A method has been developed for the microphotometric titration of test materials in ultraviolet light, taking as an example the determination of iron. The relative experimental error is about 0.5%.

A description is given of the design of a microtitrator for carrying out microphotometric titration in ultraviolet light, the end point being recorded.

The method used for determining iron has been tested on samples of bronze, a manganese concentrate, and an ore.

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*Original Russian pagination. See C. B. translation.

N,N'-DI-(2-HYDROXY-5-SULFOPHENYL)-C-CYANOFORMAZINE AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF GALLIUM

M. I. Ermakova, N. L. Vasil'eva, and I. Ya. Postovskii

Institute of Chemistry, Academy of Sciences, Ural Branch, Sverdlovsk

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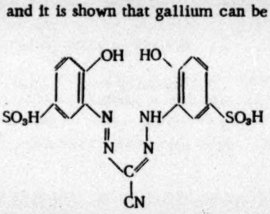
Formazine contains the tetrazo group: $Ar-N=N-C=N-NH-Ar$ in its molecule. Wizinger and co-workers [1-2] have synthesized a series of formazines. The most interesting formazines are those which contain carboxyl or hydroxyl groups in the ortho position to the tetrazo group, since they form complexes with five- or six-membered rings with metal ions. The substituent located on the meso carbon atom affects the properties of the compounds formed. Thus, compounds formed with formazines which contain the cyano group $(-N=N-\underset{\underset{CN}{|}}{C}=N-NH-)$ in the meso position are characterized by their high stability towards acids.

The capacity of formazines to form complex compounds with metals has not yet been used sufficiently in analytical chemistry. The present article contains a description of a method for synthesizing N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine [1]* and it is shown that gallium can be photometrically determined by means of this reagent.



Synthesis of N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine. 6.0 g (0.031 mole) of 2-amino-1-phenol-4-sulfonic acid is suspended in 6 ml of concentrated hydrochloric acid, and is diazotized at room temperature with a solution of 3.0 g sodium nitrite in 10 ml of water. 3.4 g (0.032 mole) of sodium cyanoacetate is dissolved in 30 ml of a 20% sodium hydroxide solution, and is coupled at room temperature with the diazotized 2-aminophenolsulfonic acid. The solution is left overnight, after which it is acidified with glacial acetic acid until the red precipitate ceases to separate out. The latter is filtered off, dried in air on a porous plate, and recrystallized from dilute (1 : 1) ethanol. The product obtained is boiled for 10 min with glacial acetic acid, and again recrystallized from dilute ethanol, and dried at 120°. 2.9 g (36.1%) of the formazine is obtained in the form of its disodium salt. The fine brown-red, hygroscopic needles, which do not melt up to 250°, are readily soluble in water and ethanol, and are insoluble in ether, benzene, acetone, carbon tetrachloride, and chloroform. Acid solutions of the compound have an orange color, while alkaline solutions are violet in color.

Found %: N 14.16; 14.40; S 13.66; 13.25. $C_{14}H_9O_8N_5S_2Na_2$. Calculated %: N 14.43; S 13.20.

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*This compound is mentioned in a review article [1], which also contains references to Swiss patents 245, 475 (July 16, 1945) and F. P. 930, 624 (July 16, 1946).

TABLE 1

The Reaction of N,N'-Di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine with Cations as a Function of the pH of the Medium

Element	pH at which the color of the formazine solution starts to change	Element	pH at which the color of the formazine solution starts to change
Copper	< 2.0	Vanadium (V)	2.2
Titanium	< 2.0	Uranium (VI)	3.0
Gallium	2.2	Iron (II)	3.0
Nickel	2.2	Iron (III)	3.0
Cobalt	2.2	Bismuth	3.5
Vanadium (III)	2.2	Tin (VI)	3.5
Zinc	4.0	Chromium (III)	5.0
Indium	4.0	Magnesium	5.0
Germanium	4.0	Calcium	5.0
Aluminum	4.5	Arsenic (III)	> 5.0
Lead	4.5	Arsenic (V)	> 5.0
Cadmium	4.5		
Manganese (II)	5.0		

Formazine forms soluble, colored compounds with metal ions. The color change of formazine solutions, which is determined by its interaction with cations, is most clearly expressed in acid media, in which the orange color of the formazine solution, in the presence of most cations, changes into blue or violet. Under such conditions, the color change of the solution in the presence of cations depends on the pH (Table 1).

Buffer solutions (acetate-hydrochloric) with pH intervals of 1 were used. The concentration of the cations in solution was about 0.001 M. The solutions were kept at room temperature for 20 hr. The color change of the solutions was observed visually.

It follows from the results given in Table 1 that at pH 3 a change in the color of the formazine solution is caused by only a small number of elements, in particular, gallium. In this connection we thought it would be of interest to test N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine as a reagent for gallium, particularly in view of the fact that there is only a comparative small number of sensitive reagents possessing sufficient selectivity which are available for the determination of this element [3, 4].

A study of N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine as a reagent for gallium. The reaction of gallium with N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine (henceforth referred to as formazine) was studied in acetate-hydrochloric solutions; the pH was controlled by means of a glass electrode. Aqueous solutions of formazine were used in the course of the work; such solutions are completely stable for two weeks. Standard gallium solutions were prepared by dissolving chemically pure gallium metal in hydrochloric acid.

The light absorption of formazine and of its compound with gallium was studied within the pH range 2-7.5 on the SF-2M recording spectrophotometer in the wavelength range 400-700 mμ. Water (twice distilled) was used as the reference solution. Solutions with equimolar concentrations of gallium and formazine: [Ga] = [Formazine] = $= 2.2 \times 10^{-5}$ M were used in the experiments. The solutions were kept for two hours at 60° and then cooled to room temperature over an hour period. Results of the optical density measurements are given in Fig. 1. Over the pH range 2-4, the absorption band of the compound remains constant; at higher pH values it shifts to the shorter wavelength side, and the shape of the curves alters. This phenomenon would suggest the existence of at least two complex gallium compounds in the system.

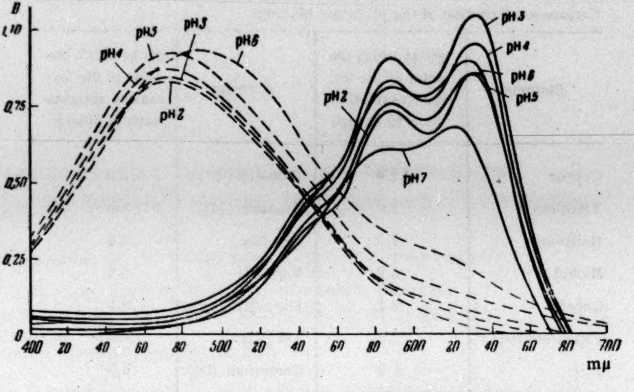

Fig. 1. Absorption curves of solutions of N,N'-di-(2 hydroxy-5-sulfophenyl)-C-cyanoformazine and of its compound with gallium. Solid lines) gallium compound: [Ga] = [formazine] = 2.2×10^{-5} M; dotted lines) formazine: 2.5×10^{-5} M; SF-2M spectrophotometer; $l = 2$ cm.

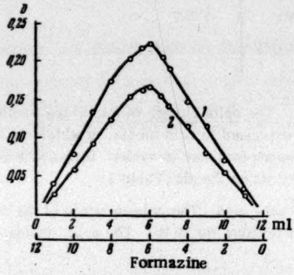

Fig. 2. Determination of the composition of the compound of gallium with N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine. 1) pH 3; 2) pH 6; SF-2M spectrophotometer; $l = 2$ cm; Σ Ga + formazine 5×10^{-6} M; $\lambda = 634$ mμ.

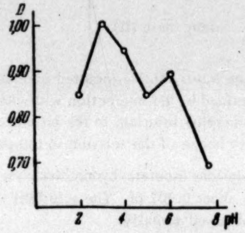

Fig. 3. The effect of pH on color development. SF-2M Spectrophotometer; $l = 2$ cm; [Ga] = [formaine] = $= 2.2 \times 10^{-5}$ M; $\lambda = 634$ mμ.

The absorption band of formazine itself also shifts with changes in the pH; this is related to the existence of different ionic forms of formazine which develop in solution with changes in the acidity. At pH < 4 formazine only dissociated through its sulfo sulfonate groups, and only one type of ions is present in solution, the absorption curves at pH 2, 3, and 4 (Fig. 1) have the maximum in the same position. At pH > 4 dissociation of formazine through its phenolic hydroxyl groups becomes possible, and new types of ions are formed in solution; as a result of this, in the given pH range, there is observed a shift in the absorption curves of formazine to the long wavelength side of the spectrum.

Within the pH range 2-5, formazine hardly absorbs light at all at 634 mμ, i.e., at the wavelength at which maximum absorption is observed in the case of its compound with gallium. Accordingly, this region of the spectrum is the most suitable for the photometric determination of gallium.

TABLE 2

Effect of Temperature on the Rate at which the Optical Density Becomes Constant

Temperature, °C	Time for equilibrium to be established, hr	Optical density of solutions cooled to 20°
85—90	0,5	0,568
70—75	1	0,566
65—60	2	0,570
50—45	6	0,568
30 - 40	10	0,566
18—20	20—34	0,566

The molar ratios which obtain during the interaction of gallium with formazine were established by the "continuous change" method [5] at pH 3 and 6. The original solutions of gallium salt and formazine had a concentration of 5.0×10^{-6} M. The mixtures were kept at 60° for two hours and then at room temperature for one hour. The optical density was measured at 634 mμ. At the same time the optical density of solutions of formazine of the same concentration was measured. The experimental results are shown graphically in Fig. 2, in which the optical densities of the mixtures, corrected for the absorption of formazine, are plotted along the ordinate. As is evident from Fig. 2, maximum absorption of the solutions, both at pH 3 and at pH 6, is observed when 1 mole of formazine corresponds to 1 g. atom of gallium. Thus, the composition of the gallium compound formed does not depend on the acidity of the medium, and the shift of the absorption curve at pH 6 (Fig. 1) can only be the result of a change in the structure of the compound. It is highly probable that at this pH the coordinated ion is different from the dissociated form of formazine observed at pH 3.

TABLE 3

Optical Density of Solutions with Variable Concentrations of Gallium Ions

Molar ratio Ga : R*	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D
1 : 1	0,568	2 : 1	0,575	5 : 1	0,606	10 : 1	0,628	20 : 1	0,635
1 : 1	0,563	2 : 1	0,594	5 : 1	0,606	10 : 1	0,633	20 : 1	0,625
1 : 1	0,568	2 : 1	0,586	5 : 1	0,594	10 : 1	0,625	20 : 1	0,630
Mean $D_{equilib}$	0,566		0,585		0,602		0,629	D_{max}	0,630

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*R⁻ formazine molecule.

The formation of a compound between gallium and formazine at another ratio differing from 1 : 1 is apparently possible, when excess complexing agent is used, as indicated by the asymmetric branch of the curve on the composition–property diagram (Fig. 2).

The results of a study of the effect of the pH on the optical density of solutions of the compound of gallium and formazine at a molar ratio of 1 : 1 are shown in Fig. 3. Prior to the measurements, the solutions were kept for two hours at 60° and then for an hour at 20°. The existence of maxima at pH 3 and 6 on the pH–optical density curve (Fig. 3) once again confirms the possibility of the formation of two different compounds of gallium, depending on the pH of the medium.

In our subsequent work gallium was determined photometrically at pH 3, since at this pH the reagent exhibits its highest sensitivity (Fig. 3), and also its highest selectivity (Table 4).

The rate at which the color develops is strongly dependent on temperature. While maximum light absorption is observed after only half an hour at 85-90°, at room temperature it is observed after 20 hr.

The effect of temperature on the rate at which equilibrium is established was studied using solutions containing gallium and formazine in a molar ratio of 1 : 1, at pH 3. The optical density of the solutions was measured at 20°. In experiments where heating was necessary, the solutions were cooled to 20° and kept for one hour at this temperature prior to optical density measurements. The color intensity of cooled solutions with a pH of 2-4 does not change for a long time; the color intensity of solutions with pH > 5 appreciably weakens with time. The relationship between the rate at which the reaction equilibrium is established and the temperature is shown in Table 2.

TABLE 4

Determination of Gallium with N,N'-Di-2-hydroxy- 5-sulfophenyl)-C-cyanoformazine in the Presence of Zinc and Aluminum

Taken, μg	Found, μg	Error (relative), %	Taken, μg	Found, μg	Error (relative), %
Ga—1,40	1,40	0,00	Ga—1,40	1,40	0,00
Ga—1,40	1,40	0,00	Ga—1,40	1,40	0,0
Al—13 600	—		Zn—2 520	—	
Ga—1,40	1,38	−1,81	Ga—1,40	1,40	0,0
Al—27 000	—		Zn—5 040	—	
Ga—1,40	1,44	+2,85	Ga—1,40	1,45	+2,90
Al—54 000	-		Zn—6 300	—	
Ga—1,40	1,50	+7,74			
Al—67 500	—				

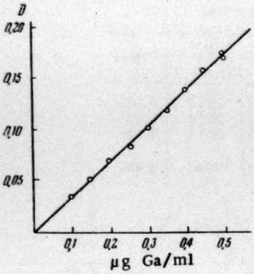

Fig. 4. Calibration curve for the determination of gallium. FÉK-M photocolorimeter; red filter; l = 1 cm.

The molar extinction coefficient was determined by the "saturation" method. The original concentration of the components was 1.25×10^{-5} M while the pH was 3.1. In order to suppress dissociation of the compound formed, excess gallium ions at the rate of 2 , 5 , 10 , and 20 times that stoichiometrically necessary were added. The solutions were kept for two hours at 60° and one hour at 20°.

The optical density was measured on a SF-2M spectrophotometer at 634 mμ in a cuvette with a layer thickness of 2 cm; water was used as the reference solution. As is evident from the results given in Table 3, dissociation of the complex is suppressed when there is only a tenfold excess of Ga^{3+} ions in solution. The value of molar extinction coefficient ε calculated from the mean value D_{max} is 25.200; this indicates that the reagent has a fairly high sensitivity.

The values of the optical density of solutions in which the dissociation of the complex compound has been suppressed, and of solutions with an equilibrium concentration, and which are shown in Table 3, were used for calculating the dissociation constant of the compound of gallium with formazine [6]: $K_{dissoc.} = \frac{\alpha^2}{1-\alpha} \cdot C$, where $\alpha = \frac{D_{max} - D_{equilib.}}{D_{max}}$ and C is the original concentration of the components in solution, equal to 1.25×10^{-5} M. The approximate value of the dissociation constant was found to be $K = 1.45 \times 10^{-7}$.

Aqueous solutions of the compound of gallium with formazine do not opalesce in ultraviolet light, and conform the Beer's law up to gallium concentrations of 2.5 μg/ml. Under the conditions established (pH 3, 634 mμ) the minimum gallium concentration which can be determined is 0.05 μg/ml (for a layer thickness of 1 cm).

The compound is not extracted by ether, butyl and isoamyl alcohols, ethyl and amyl acetate, methyl ethyl ketone, hexanone, carbon tetrachloride, or benzene; it is readily soluble in water and alcohol.

Copper, nickel, cobalt, titanium, vanadium, and iron interfere with the photometric determination of gallium with formazine. At the same time, aluminum and zinc do not form colored compounds with formazine, and, accordingly, do not interfere with the determination of gallium.

The results obtained (Table 4) show that the reagent permits determination of down to 0.002 % of gallium in aluminum, and down to 0.02% in zinc.

Determination of small amounts of gallium in aluminum.* An aliquot of aluminum metal (0.05-0.10 g) is dissolved in hydrochloric acid (1 : 1) by heating on a water bath, and the solution evaporated to a small volume (but not to dryness). The sirupy mass is washed into a graduated cylinder with an amount of 1 M sodium acetate such that the total volume of the liquid in the cylinder is 15 ml. By adding the appropriate amount of 1 M hydrochloric acid and 1 M sodium acetate solution, the requisite acidity is established (pH 3), using a glass electrode. The volume of the solution is adjusted to 20 ml with a solution of an acetate-hydrochloric buffer solution with a pH of 3 (50 ml of 1 M CH_3COONa and 48.5 ml of 1 M HC), 1.5 ml of a 0.5% aqueous solution of formazine is added, and the solution left overnight at room temperature. The optical density is measured at 634 mμ on a SF-2M or FÉK-M spectrophotometer with a red filter, relative to the same solution free from gallium; the layer thickness is 2 cm. The gallium concentration is determined from a calibration curve. The latter is constructed by measuring the optical density of acetate-hydrochloric acid solutions (pH 3) containing from 0.1 to 1.5 ml of 0.0001 M $GaCl_3$ solution in 20 ml (at 0.1 ml intervals), 2 ml of 1 M $AlCl_3$ solution free from gallium,** and 1.5 ml of a 0.5% solution of formazine.

SUMMARY

A description is given of the synthesis of N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine.

The possibility has been demonstrated of using N,N' di-(2-hydroxy-5-sulfopheny)-C-cyanoformazine for the photometric determination of gallium. At pH 3 the absorption band of the compound (634 mμ) is far removed from the absorption band of formazine (470 mμ); the molar extinction coefficient at pH 3 and 634 mμ is 25,200. Solutions of the compound conform to Beer's law within the range 0.050-2.5 μg Ga/ml.

It has been shown that N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine permits the determination of gallium in aluminum and zinc at a ratio of Ga : Al = 1 : 50,000 and Ga : Zn = 1 : 5,000.

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*When aluminum contains impurities which interfere with the determination of gallium, such as copper or iron, it is necessary to remove the gallium, e.g., by extracting it with ether from hydrochloric acid solutions [7].

**Aluminum chloride is purified from gallium by precipitating the latter with cupferron from weakly acid solutions together with iron [8].

***Original Russian pagination. See C. B. translation.

A FLOTATION METHOD FOR STUDYING THE EFFECT OF RUBIDIUM PRESENT AS AN IMPURITY ON THE DENSITY OF KCl CRYSTALS, AND THE DETERMINATION OF THE RUBIDIUM CONTENT OF POTASSIUM SALTS

V. S. Rylov

Physico-Technical Institute, Academy of Sciences of the USSR, Leningrad

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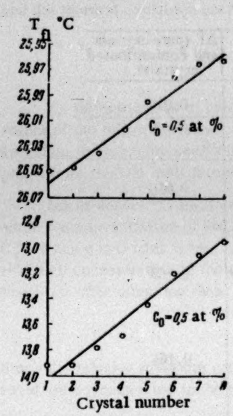
The flotation method of analysis is based on a comparison of the densities of two crystalline samples by measuring the flotation temperature (neutral equilibrium temperature) of the crystals in an indifferent liquid. The flotation method has been successfully used for analyzing the isotopic composition of several chemical elements, and enables a high accuracy to be achieved with simple equipment. Since the impurities present in crystals affect their density, the flotation method can be successfully applied to the study of the effect of impurities on the crystal density. The change in the density of the crystals from the true value can, in some instances, enable one to determine the concentration of the impurity in the original material and in crystals obtained from this material; it is possible to assess the changes in the crystalline lattice, and whether or not the impurity is isomorphous with the main component of the crystal. When, during the growth of the crystals, the impurity passes from the mother liquid into the crystals so that there is a change in the original concentration, the flotation method permits determination of the partition coefficient (distribution) of the main component and the impurity.

The present article is devoted to a description of the application of the flotation method for the determination of rubidium present as an impurity in potassium salts, and for the study of the effect of rubidium on the density of KCl.

The technique of the flotation method has been considered earlier [1].

Determination of the partition coefficient of potassium and rubidium during crystallization of a KCl melt containing rubidium as impurity. a) Purification of KCl and RbCl from impurities. In order to determine the partition coefficient it was necessary to have a KCl salt with a total concentration of impurity of $< 10^{-3}$ at.%, and to have a RbCl with a content of impurity < 0.1 at%. It was established spectrographically that potassium salts (KCl, KNO_3), chemically pure and analytical grade reagents produced by the Russian chemical industry, contain about 10^{-3} at.% rubidium. In order to cut down the rubidium content as well as the content of other elements in the potassium salts, KCl (chemically pure) was recrystallized five times from an aqueous solution, 25% of the crystalline phase being chosen in each operation. According to Hutchinson [2] purification of KCl by recrystallization ensures preparation of a salt with the requisite purity. Feit and Kubierzhskii [3] found that after 30 recrystallizations of carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$) the mother liquor is enriched with rubidium from 0.02 to 9.5 at%.

In order to establish the extent of purification of KCl from rubidium, an experiment was carried out in which 12 successive crystallization operations were made by cooling a saturated solution at 60° to 20°. After each recrystallization 73-75% of the KCl remained in the mother liquor. The crystalline phase was rejected. In the original salt the rubidium concentration was $C_0 = 0.001$ at%, while in the final solution (after 12 recrystallizations) it increased



The relation between T_{fl} of contaminated crystals as a function of the series number of the crystal during extraction from the salt melt.

to $C'' = 0.01$ at.%. The partition coefficient α was determined from the relation (see [4]):

$$\alpha^n = C''/C_0$$

where n is the number of the degree of separation, corresponding to 12 crystallization operations, in which 73-75% of material from the mother liquor was taken. Calculation gives (see [4]) for this factor the value $n = 3.6$. From which we find that: α is about 1.9. Since, during the purification, it was necessary to remove rubidium from KCl, the mother liquor after each precipitation was rejected. In the range 60° to 20° about 25% of the salt crystallized out; this corresponds to a degree of separation of about 0.7. From the preceding calculations it is evident that in order to change the rubidium concentration ten times, a degree of separation of 3.6 is required. Since one crystallization operation corresponds to a degree of separation of 0.7, five operations should be sufficient for preparing KCl crystals containing about 10^{-4} at.% rubidium. In this way 10 g of KCl was prepared which contained less than 10^{-3} at.% of Na and Ca and about 10^{-4} at.% Rb according to spectrographic analysis.

RbCl was purified from impurities by the ionic mobility technique according to a technique described earlier [5].

b) Experimental procedure. In order to determine the partition coefficient α for potassium and rubidium during crystallization of a chloride melt, five samples of KCl freed from impurities were prepared. RbCl was added to four of these samples in such an amount that its concentration in the samples was as follows:

Sample No. 1 $C_0 = 5.0$ at. %
Sample No. 2 $C_0 = 0.5$ at. %
Sample No. 3 $C_0 = 0.05$ at. %
Sample No. 4 $C_0 = 0.005$ at. %
Sample No. 5 $C_0 = 0.000$ at. %

From each sample 5-8 crystals with a weight of q = 12-14 mg were prepared by a method described in [1]. The crystals were grown from salts fused at 780° in a platinum crucible. The original amount of salt Q in the crucible was determined by weighing. The crystals from each sample containing rubidium were floated together with crystals from sample No. 5. The flotation temperature T_{fl} of the pure crystals was compared with T_{fl} of a quartz float; this made it possible to assess the reproducibility of the density of pure crystals from one experiment to the other. Crystals from samples Nos. 1-4 were grown as equal in size as possible. Marks were made on some of them (see [1]) in accordance with the series number of the crystal during their growth.

It follows from Table 1 that the rubidium present as impurity appreciably depresses T_{fl} of the crystals as compared with T_{fl} of pure crystals. Accordingly, the density of KCl increases with increasing RbCl concentration. At a concentration of $C_0 = 0.005$-0.05 at.%, the density of the contaminated crystals is independent of the number of the crystal in individual experiments (see Expts. Nos. 1-4). For $C_0 = 0.5$-5.0 at.%, T_{fl} of the contaminated crystals is already dependent on the series number of the crystal (see Expts. Nos. 5-6); it decreases with the increase in the series number of the crystal. It is clear from column 7, Table 1, that the reproducibility of T_{fl} of the pure crystals relative to the float is fairly good. In Expts. 5 and 6, the crystals were floated in 1,3-dibromopropane to which ethylene bromide had been added; accordingly the values of the differences in the flotation temperatures of the pure crystals and float are different to those in Expts. Nos. 1-4. In column 8, the difference ΔT between crystals from pure KCl and from contaminated crystals is calculated for Expts. 5 and 6, using only T_{fl} for the crystals corresponding to the first two series numbers. T_{fl} was determined by means of a Beckmann thermometer, the scale of which was accurate to ± 0.1°C.

In the diagram is shown a curve relating T_{fl} of crystals in Expts. 5 and 6 to the series number of the crystal. The difference between the flotation temperatures of two adjacent crystals, $\Delta t = \left[\frac{\text{degree C}}{\text{1 crystal}}\right]$, necessary for the calculations, is determined from the slope of the straight lines.

TABLE 1

Expt. No.	C_0, at.%	Q.mg	Crystal number	T_{fl} of contaminated crystals, °C	T_{fl} of pure crystals, °C	ΔT_{f-p} (float - pure crystals)	ΔT (pure crystals and contaminated crystals)
1	0,005	360	1	13,278	13,293	0,323	0,015
			2	13,278	13,293		
			3	13,278	13,293		
			4	13,280	13,294		
			5	13,275	13,291		
2	0,005	360	1	13,283	13,296	0,323	0,016
			2	13,283	13,296		
			3	13,283	13,300		
			4	13,282	13,302		
			5	13,285	13,303		
3	0,05	360	1	13,129	13,293	0,323	0,163
			2	13,129	13,293		
			3	13,129	13,293		
			4	13,129	13,294		
			5	13,132	13,291		
4	0,05	360	1	13,133	13,296	0,323	0,164
			2	13,134	13,296		
			3	13,136	13,300		
			4	13,137	13,302		
			5	13,136	13,303		
5	0,5	360	1	26,050	27,483	−1,362	1,434
			2	26,047	14,483		
			3	26,035	27,483		
			4	26,017	27,482		
			5	25,995			
			6	25,975			
			7	25,965			
			8	25,961			
6	5,0	300	1	13,905	27,483	−1,362	13,585
			2	13,890	27,483		
			3	13,788	27,483		
			4	13,695	27,482		
			5	13,427			
			6	13,201			
			7	13,072			
			8	12,942			

TABLE 2

C_0	0,005	0,05	0,5	5,0
ΔT, °C	0,016∓0,002	0,164∓0,002	1,435∓0,005	13,585∓0,100
$\Delta T_{\text{true}} = \Delta T \left(1 - \frac{\beta_k}{\beta_{\text{liq.}}}\right)$	0,014∓0,002	0,143∓0,002	1,260∓0,005	11,9∓0,1
$K = \frac{\Delta T_{\text{true}}}{C_0}$	2,7∓0,4	2,86∓0,04	2,52∓0,01	2,38∓0,02

In Table 2 are given the mean values of ΔT, taken from Table 1, and the values of ΔT_{true} calculated from ΔT taking into account the thermal expansion of the flotation liquid and the crystals.

Assuming that RbCl present as an impurity in KCl up to a concentration of 5 at.% and addition of ethylene bromide to 1,3-dibromopropane insignificantly affect the thermal expansion coefficient of the KCl crystals and of the flotation liquid, in subsequent calculations the thermal expansion coefficient of 1,3-dibromopropane:

and the thermal expansion coefficient of KCl were used:

$$\beta_{\text{liquid}} = 902\cdot 10^{-6}\,\frac{1}{\text{deg C}} \qquad [1]$$

c) Determination of partition coefficient. As a result of measurements and preliminary calculations the values of the following factors were obtained: Q, q, C_0, Δt, ΔT. On the basis of these results it is possible to calculate the partition coefficient of potassium and rubidium which determines the extent to which the rubidium passes from the salt melt into the crystals.

Let us denote the RbCl concentration in the crystal grown by C'_n, where n is the series number of the crystal, while the concentration of RbCl in the fused salt immediately after the growth of the given crystal is denoted by C''_n. When $q \le Q$ (this is true for the experiments given in Table 1), it can be assumed approximately that the rubidium concentration in the first two crystals differs insignificantly, while the concentration of rubidium in the fused salt after removing these crystals:

$$C''_1 \simeq C''_2 \simeq C_0. \qquad (1)$$

Since the relative rubidium content in KCl is low, the partition coefficient can be written as the ratio of the rubidium concentration in the crystal and in the fused salt:

$$\alpha = C'/C''. \qquad (2)$$

For the first two crystals, according to [1],

$$\alpha = C'/C_0. \qquad (3)$$

Rayleigh's relation (see, e.g.,[4]), which relates the partition coefficient to the concentration and amount of material in the residual fused salt, can be written as:

$$C''_n = C_0\left(\frac{Q''_n}{Q}\right)^{\varepsilon}, \qquad (4)$$

where $\varepsilon = \alpha - 1$, $Q''_n = Q - nq$. From (2) and (4) we find that

$$C'_n = \alpha C_0\left(\frac{Q-nq}{Q}\right)^{\varepsilon}.$$

From which

$$C'_{n+1} - C'_n = \alpha C_0\left[\left(\frac{Q-(n+1)q}{Q}\right)^{\varepsilon} - \left(\frac{Q-nq}{Q}\right)^{\varepsilon}\right]. \qquad (5)$$

In contrast to $K = \dfrac{\Delta T_{\text{true}}}{C_0}$ (see Table 2) the ratio of ΔT_{true} to the RbCl concentration in the first crystal gives the true proportionality coefficient, i.e.

$$K_{\text{true}} = \frac{\Delta T_{\text{true}}}{C'_1}. \qquad (6)$$

Or, using (3), we have:

$$K_{\text{true}} = \frac{\Delta T_{\text{true}}}{\alpha\cdot C_0}. \qquad (6a)$$

From this, the difference between the concentrations of the first and second crystals will be:

$$C'_2 - C'_1 = \frac{-\Delta t_{\text{true}}}{K_{\text{true}}} = \frac{-\Delta t_{\text{true}}}{\Delta T_{\text{true}}}\alpha C_0. \qquad (7)$$

where

$$\Delta t_{\text{true}} = \Delta t \left(1 - \frac{\beta_k}{\beta_{\text{liquid}}}\right).$$

Equating (5) and (7), we have:

$$\frac{\Delta t_{\text{true}}}{\Delta T_{\text{true}}} = \frac{\Delta t}{\Delta T} = \left(\frac{Q-q}{Q}\right)^{\varepsilon} - \left(\frac{Q-2q}{Q}\right)^{\varepsilon}. \tag{8}$$

The first part of expression (8) can be resolved into a McLauren's series in the ε'th degree, by confining it to the first member of the resolution (the second member only introduces a negligible correction). After transformation, we have:

$$\frac{\Delta t}{\Delta T} = \varepsilon \ln \frac{Q-2q}{Q-q}. \tag{9}$$

Using equation (9), it is easy to calculate the partition coefficient $\alpha = 1 + \varepsilon$ for Expts. 5 and 6.

For Expt. 5: $C_0 = 0.5$ at.%, $\Delta t = 0.015 \dfrac{\text{deg C}}{\text{crystal}}$, $\Delta T = 1.434°$

$Q = 360$ mg, $q = 14.5$ mg.

From which $\alpha = 0.76$.

For Expt. 6: $C_0 = 5.0$ at.%, $\Delta t = 0.158 \dfrac{\text{deg C}}{\text{crystal}}$, $\Delta T = 13.58°$

$Q = 300$ mg, $q = 12.5$ mg.

From which $\alpha = 0.74$.

From the calculated values of α it follows that rubidium enters the crystal phase of the KCl, increasing thereby its concentration by $1/\alpha$ for one separation step.

The accuracy with which α is determined depends mainly on the accuracy with which the crystals are weighed, and on the accuracy of the determination of Δt. In our previous calculations the mean value of Δt was calculated for eight crystals, i.e., it was assumed that the flotation temperatures of the crystals changes linearly with the increase in the series number of the crystal. In actual fact, as is evident from Eq. (9), the value of Δt increases with the increase in the crystal number (see Fig. 1). It follows from this that a more accurate value of α can be obtained by determining the slope of the tangent and the curve at the origin. In the previous experiments, as is evident from the curve (Fig. 1), this could not be done because of the scatter in the values of T_{fl}. This scatter can be explained by the fact that the size of the crystals is not constant enough. An assessment carried out on the basis of Eq. (9) shows that a mean value of Δt obtained on the basis of eight crystals of equal size ($q = 10$ mg, $Q = 400$ mg) will be greater than Δt for the first two crystals by 10-15%.

There is still another possible source of error, which is related to insufficient mixing of the molten salt during the growth of the crystal. When the melt is not adequately stirred it is necessary to grow crystals at the minimum growth rate.

Effect of RbCl on the density of KCl crystals. The values of ΔT_{true} characterize the changes in density as a function of rubidium concentration. Let us assume that for a value of $C_0 \leq 5$ at.%, the coefficient K_{true}, which depends on the packing of the rubidium ions in the KCl lattice, remains constant, i.e., that the packing coefficient is independent of the concentration, within the limits indicated. For Expts. 5 and 6 it is possible to calculate by means of Eq. (6a) that the value of $K_{\text{true}} = 3.3 \pm 0.4$. In Table 2 are given the values $K = \alpha \cdot K_{\text{true}}$, which increase with decreasing concentration C_0. Taking $K_{\text{true}} = 3.3$ to be constant, it is possible to calculate the values of α for Expts. 1-4 and to find C' by means of (3). The corresponding values are given in Table 3.

If the density of pure KCl crystals is denoted by ρ_0, while the density of contaminated crystals is denoted by ρ', it is possible to write:

$$\rho' - \rho_0 = \Delta\rho = \rho_0 (\beta_{\text{liquid}} - \beta_k) \Delta T, \tag{10}$$

TABLE 3

C_0, at. %	α	C', at. %
5,0	0,74	3,7
0,5	0,76	0,38
0,05	0,88	0,044
0,005	0,8–0,9	0,004–0,005

TABLE 4

C', at. %	3,7	0,38	0,044	0,004
γ	0,00578	0,00596	0,00585	0,0058

where ΔT is the difference in the flotation temperatures of these crystals. At the same time we have:

$$\Delta \rho = \gamma \cdot C', \tag{11}$$

where γ is a constant coefficient.

From (10) and (11) we find

$$\gamma = \frac{\rho_0 (\beta_{\text{liquid}} - \beta_1)\ \Delta T}{C'} \tag{12}$$

where $\rho_0 = 1.988\ \text{g/cm}^3$. By means of (12) and using the results from Tables 2 and 3, the values of γ for various concentrations are calculated.

It follows from Table 4 that γ = const. From which relation (11) is linear, i.e.

$$\Delta \rho = 0.6 \cdot 10^{-2} C'\ \text{g/cm}^3,$$

where C' is in at.%.

It is interesting to note that Pick and Weber have also established a linear relation between the density of KCl and the concentration of $CaCl_2$ present as an impurity [6].

$$\Delta \rho = -0.8 \cdot 10^{-2} C'\ \text{g/cm}^3,$$

where C' is the concentration in at.%, the maximum value of which in these experiments was 2×10^{-2} at.%.

Knowing the experimental value $K_{\text{true}} = \Delta T / C'_1 = 3.3$, it was interesting to compare it with the corresponding coefficient calculated on the assumption of the independence of the packing of the Rb^+ ions on the concentration in the KCl crystal lattice. Let us denote the calculated coefficient by $K_{\text{calc.}}$. Further, let the flotation temperature of pure crystals be denoted by T_0, while that of crystals contaminated with rubidium be T_1. For the given values of T_0 and T_1 the densities of the crystals coincide with the density of the flotation liquid; accordingly it is possible to write:

$$\rho_0 = \frac{\mu_0}{V_0 (1 + \beta_k \cdot T_0)} = \rho_{\text{liquid}} (1 - \beta_{\text{liquid}} \cdot T_0), \tag{13}$$

where μ_0 is the molecular weight of KCl, V_0 is the molecular volume of KCl at 20°, ρ_{liquid} is the density of the flotation liquid at 20°, and ρ_0 is the density of pure KCl crystals.

$$\rho_1 = \frac{\mu_0 (1 - C') + \mu_1 C'}{[V_0 (1 - C') + V_1 \cdot C'] (1 + \beta_k T_1)} = \rho_{\text{liquid}} (1 - \beta_{\text{liquid}} \cdot T_1), \tag{14}$$

where μ_1 is the molecular weight of RbCl, V_1 is the molecular volume of RbCl in the KCl crystals, and $100 \cdot C'$ is the RbCl concentration in at.%.

Subracting Eq. (13) from (14) we find:

$$\Delta T = T_0 - T_1 = \frac{\left(\frac{\mu_0}{V_0} - \frac{\mu_1}{V_1}\right) V_1 \cdot C'}{\rho_{\text{liquid}} (\beta_k\ \beta_{\text{liquid}}) \cdot V_0}\ 10^{-2}. \tag{15}$$

From which:

$$K_{\text{calc.}} = \frac{\Delta T}{C'} = \frac{\frac{V_1}{V_0}\left(\frac{\mu_1}{V_1} - \frac{\mu_0}{V_0}\right)}{\rho_{\text{liquid}}(\beta_{\text{liquid}} - \beta_k)} 10^{-2} \tag{16}$$

Equating $K_{\text{calc.}} = K_{\text{true}} = 3.3$, and substituting in (16) the known values of $\rho_{\text{liquid}} = 1.985$ g/cm³, $\rho_0 = 1.988$ $= 1.988$ g/cm³, and $V_0 = 37.45$ cm³/ mole, it is possible to calculate the molecular volume of RbCl which can be assigned to it in the KCl crystal, if, thereby, the molecular volume of KCl does not change. Calculations based on (16) give for V_1 a value of 51 ± 1 cm³/mole: at the same time it is known that the molecular volume of RbCl is equal to 43.2 cm³/mole.

Accordingly, the presence of rubidium ions in the crystal lattice of KCl leads to a deformation of the lattice, the size of the latter being increased. Under these conditions the expansion of the crystal lattice is relatively small, since the density of the contaminated crystal also continuously increases with increasing RbCl concentration.

Determination of the rubidium concentration in potassium by the flotation method. The sensitivity of the flotation method for a certain impurity concentration will be very high. In fact, it is clear from Table 2 that a change of 0.001 at.% of rubidium in KCl crystals leads to a change in T_{fl} of 0.003°, which corresponds to a change of about 3 γ in the density of KCl. In general, the flotation method is applicable to the quantitative analysis of any two chemical compounds which form between them solid solutions in the concentration range we are interested in. The flotation method includes the following operations:

Preparation of standard samples with a known relative content of both chemical compounds; growth of crystals from the standard samples; the choice of a flotation liquid which is chemically neutral to the crystals and similar to them in density; determination of the thermal expansion coefficient of the liquid and the crystals (a very simple and accurate flotation method has been developed for crystals [7]). Further, by floating the crystals, the relation between T_{fl} of the crystals and the concentration of the components is established, and a calibration curve is constructed.

Determination of the relative contents of the two components in the test material. For this purpose the material should be purified from foreign impurities to the same condition as the standard samples. Crystals are then prepared and their T_{fl} determined relative to that of the standard crystals (or with respect to quartz floats). The concentration of both components is finally found from the calibration curve.

Let us consider the technique for the determination of the rubidium concentration of rubidium in potassium. The curve relating the flotation temperature of contaminated crystals ΔT and the rubidium concentration in the crystals – C' – is found from (6) and from Table 2, i.e.

$$C' = \frac{\Delta T}{K_{\text{true}}}\left(1 - \frac{\beta_k}{\beta_{\text{liquid}}}\right) \tag{17}$$

When 1,3-dibromopropane is used as the flotation liquid, Eq. (17) is written:

$$C' \text{ (at.\%)} = 0.27 \cdot \Delta T \text{ (deg C)}$$

A mixture of ethylene bromide and chlorobenzene can also be used as a flotation liquid. The thermal expansion coefficient of this mixture can be calculated with reasonable accuracy from the known thermal expansion coefficients of ethylene bromide and chlorobenzene, on the basis that these values are additive.

At a certain rubidium concentration of the original salt, it is necessary to take into account the partial separation of rubidium and potassium which during the growth of crystals from a molten salt, i.e.

$$C_0 = \frac{C'}{\alpha} = \frac{\Delta T}{K}\left(1 - \frac{\beta_k}{\beta_{\text{liquid}}}\right) \tag{18}$$

In Table 2 are given the values of K found for different rubidium concentrations. The content of other impurities amounted to $< 10^{-3}$ at.%. Naturally, the values of K can only be used in the analysis in those cases where the content of the other impurities is also $\leq 10^{-3}$ at.%. When this condition is fulfilled the accuracy with which the rubidium concentration in potassium can be determined will only depend on the accuracy with which ΔT can be read, and on the value of K (see Eq. (18)].

Using (18), on the basis of the results given in Table 2 we find that in the range 0 to 5 at.%, the absolute error in the determination C_0 amounts to ± (1-2) 10^{-3} at.%, independently of C_0. As experiments have shown, the presence of other impurities in the test salt in amounts of about 10^{-2}% correspondingly increases the error in C_0 to about 10^{-2} at.%.

Foreign impurities can be removed by the method of ionic mobilities described in [5]. When this purification method is used, rubidium, which has almost the same ionic mobility as potassium, is not removed from the salt, while the remaining impurities (cations and anions, apart from the chloride ion) are readily removed. The only exception is cesium, whose ionic mobility is also close to that of potassium. Cesium is, however, usually present as a microcomponent, and it can be ignored.

Thus, if the relationship $\Delta T(C_0)$ is known, the determination of the rubidium concentration of potassium consists of the following successive operations:

Purification of the test material from foreign impurities to the required condition. The final product is prepared in the form of the chloride, the amount necessary being about 300 mg.

Growing 4-6 crystals of KCl from the molten salt (see [1]).

Determining the flotation temperature of these crystals relative to T_{fl} of standard crystals or relative to T_{fl} of a quartz float graduated against standard crystals. And, finally, determination of the rubidium concentration C_0 from a calibration curve or from Eq. (18).

The author wishes to thank G. Ya. Ryskin for discussing the theme of the work described here.

SUMMARY

The partition coefficients of rubidium between molten KCl and the crystalline phase at about 780° for RbCl contents of 5.0 to 0.005 at.% in KCl have been determined by a flotation method. It has been shown that the partition coefficient α varies from 0.74 to 0.9, i.e., at low RbCl concentrations the transfer of rubidium into the crystalline phase occurs with less partitioning than at high concentrations.

The density of KCl crystals increases with increasing rubidium concentration according to the equation: $\Delta = 0.6 \times 10^{-2} \cdot C'$.

RbCl molecules present in KCl crystals increase the size of the crystal lattice to a greater extent than would be possible if the RbCl molecules were found in the KCl lattice with a characteristic molecular volume.

It has been shown that the flotation method can be used for the determination of rubidium concentration in potassium salts with an accuracy of up to (1-2) 10^{-3} at.%.

An assessment is made of the partition coefficient of rubidium and potassium during the crystallization of their chlorides from an aqueous solution ($\alpha = 1.9$). During this process, as is known, the rubidium concentrates in the solution.

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FLAME PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF CESIUM IN NATURAL SAMPLES ENRICHED WITH POTASSIUM

E. A. Fabrikova

Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements,
Academy of Sciences of the USSR, Moscow

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The presence of potassium as an impurity in solution increases the radiation intensity of rubidium in the flame [1-3]. This fact has been used for increasing the sensitivity of the flame photometric method of determining Cs in minerals [4]. This technique specifies the addition of 2500 μg of potassium/ml to the solution; larger amounts are undesirable, since the characteristic K radiation creates a background around the cesium wavelength, thereby depressing the sensitivity of the method.

Determination of small amounts of cesium (ten thousandths of a percent) in natural materials is only possible with large amounts of sample (a minimum of 5 g/50 ml). The optimum potassium content in this case is 2.5–3.0%. In samples which are rich in potassium, it is impossible, by simply increasing the amount of the aliquot, to increase the sensitivity of cesium determination, since with increasing cesium concentration in the test solution, the potassium concentration increases to the same extent. Determination of small amounts of cesium in such samples can only be carried out after removing the excess potassium.

We have studied the possibility of separating microamounts of cesium from macroamounts of potassium by coprecipitating cesium with sparingly soluble ammonium silicomolybdate. Of the coprecipitants used hitherto [5-8] for cesium, only thallium chloroplatinate can be used for separating it from potassium [8]. For analytical purposes, however, thallium chloroplatinate is not very suitable, since it only permits removal of not more than 80% of the cesium present in solution.

Silicomolybdic acid is one of the best precipitants for cesium. The sensitivity of this reaction, according to Moser and Ritschel [9], is 1.58×10^{-4} g/ml. The potassium salts of this acid are readily soluble.

In developing conditions for coprecipitating gamma amounts of cesium with ammonium silicomolybdate, we made use of published results [10, 11] which indicate that the solubility of cesium silicomolybdate decreases with increasing acidity of the medium; the solubility of ammonium silicomolybdate itself sharply decreases when excess ammonium chloride is present in solution. By alternately changing these factors in the presence of sodium silicomolybdate and gamma amounts of cesium in solution, and by determining the extent to which Cs is entrained by the ammonium silicomolybdate precipitated, we found that in the case of a solution containing 0.1 g H_2SO_4/ml, 0.2 g NH_4Cl/ml, and 1.4 g $2Na_2O \cdot SiO_2 \cdot 12MoO_3$/ml, cesium is completely (95-100%) entrained by the ammonium silicomolybdate which is precipitated under these conditions (Table 1).

Subsequently, we checked on the degree to which cesium is coprecipitated with ammonium silicomolybdate under the optimum conditions, in the presence of potassium. Up to 20,000 μg K/ml was added to the solution (corresponding to 20% K on dissolving 5 g of it in 50 ml of solution). It was established that the extent to which cesium is entrained (95-100%) by the ammonium silicomolybdate is independent under these conditions of the presence of potassium in the solution. Most of the potassium (99.8%) remains in solution.

TABLE 1

Coprecipitation of Cesium with Ammonium Silicomolybdate from 50 ml of Solution Containing 0.1g H_2SO_4/ml, 0.2 g NH_4Cl/ml, and 1.4 g $2Na_2O \cdot SiO_2 \cdot 12MoO_3$/ml

Amount taken for coprecipitation, μg/ml	Cs found in the precipitate dissolved in 50 ml of an ammoniacal solution, μg/ml						Cs coprecipitated, %
	expt. no.					mean	
	1	2	3	4	5		
0,2	0,19	0,2	0,17	0,21	0,20	0,19	95,0
1,0	1,0	1,1	0,9	1,0	1,0	1,0	100,0
10	10	9,9	9,8	10,2	10,1	10,0	100,0
20	19,8	20,00	20,10	19,90	20,00	19,96	99,8

TABLE 2

Control Determinations of Cesium

Sample	Potassium content of the sample, %	Cs found in the sample, %	Cs added, %	Cs found after addition, %	Relative error, %
Pegmatoid granite	4.73	0.0007	0.0007	0.0015	+ 14.1
Parfiro granite	3.5	0.0006	0.0006	0.0011	− 16.6
Biotite parfiro granite	4.5	0.0011	0.0011	0.0022	0
Biotite medium grained granite	7.13	0.0002	0.0002	0.0004	0

The completeness of removal of microamounts of cesium during the analysis of various granite rocks, using 5 g samples, and with preliminary separation of the cesium from excessive amounts of potassium by means of ammonium silicomolybdate, was demonstrated by introducing additional amounts of Cs to samples containing some ten thousandths parts of a percent of Cs, and finding the amount of cesium introduced, by difference, by carrying out determinations before and after the addition (Table 2). The maximum losses did not exceed 16.6%. The limiting sensitivity with which Cs can be determined on a flame setup in the presence of 2500 μg potassium/ml is the same as in [7], viz, 0.1-0.2 μg/ml).

The chemical preparation of the samples is described below. The technique used for carrying out flame photometric measurements has been published earlier [4].

Experimental procedure. Preparation of silicomolybdic reagent: 1) To 100 ml of a 10% NaOH solution is added 38 g of MoO_3 in small portions (1-1.5 g) with stirring until complete solution is obtained. The solution is heated before addition of each portion of MoO_3. The solution obtained should be free of precipitate.

2) The sodium silicate solution is prepared from 1.5 g of $Si(OH)_4$, 2 g of NaOH, and 50 ml H_2O.

3) Twelve ml of H_2SO_4 (sp. gr. 1.84) is mixed with 100 ml H_2O.

Initially the molybdate and silicate solutions are poured together; the sulfuric acid solution is then added slowly in small portions to the mixture obtained. The reagent may be turbid; if this is the case, it should be filtered. The reagent is bright yellow in color. Mixing is carried out in the cold.

Sample preparation. A five g sample is decomposed with a mixture of hydrofluoric, sulfuric, and nitric acids (40-50 ml HF, 10 ml H_2SO_4, and 1 ml HNO_3) in a No. 8 platinum basin. To the dry residue obtained after treatment with the acid is added 5 ml of H_2SO_4 in order to remove HF completely, and the test again evaporated to the appearance of sulfuric acid fumes. After cooling, the residue is transferred by means of 50 ml H_2O into a 100 ml beaker and the precipitate filtered off; the latter is washed with hot water. The filtrate plus the wash liquors are evaporated to a volume of 50 ml. Cesium is removed from the solution obtained at room temperature. For this purpose the solution is acidified with 3 ml H_2SO_4 (sp. gr. 1.83). After careful mixing, to the solution is added 15 ml of the silicomolybdic reagent, also with careful stirring, and, finally, to the solution obtained is added 10 g of dry, well ground NH_4Cl. During this stage the yellow precipitate of ammonium silicomolybdate separates out. After 20-30 min the precipitate is filtered through a filter ("white band"), the beaker and the precipitate are washed three times with a wash liquor which has the following composition: 500 ml H_2O, 30 ml H_2SO_4 (sp.gr. 1.84), and 100 ml NH_4Cl.

After washing, the precipitate plus filter are transferred to the same beaker and treated with 25-30 ml of ammonia solution (1 : 1), and the whole stirred until the ammonium silicomolybdate has completely decomposed; this is readily observable by the disappearance of the yellow precipitate. The filtrate is immediately filtered into a standard flask (50 ml). To it is added 5 ml of a K_2SO_4 solution containing 25,000 μg K/ml and the volume made up to the mark with water. Cesium is finally measured flame photometrically by means of the technique described previously [4]. A correction should, however, be made in this case, both for the standard and for the test solutions, by measuring the mean radiation which is detected by the apparatus on rotating the drum of the monochromator 7-10° on both the long wavelength and short wavelength side of the cesium line (852.1 mμ).

The standard reference solution is treated in exactly the same way as the solution of the sample. For this purpose, 50 ml of a Cs_2SO_4 solution is taken, whose cesium content is accurately known and is of the order of 1.5 μg Cs/ml. The solution is acidified with 3 ml of H_2SO_4, after which the cesium is coprecipitated as described above in the case of the test sample. The coprecipitation operations are carried out simultaneously for several samples and for one standard solution. A blank test is also necessary.

The suggested method, in which cesium is coprecipitated with ammonium silicomolybdate, can also be used for the flame photometric determination of small amounts of cesium in potassium salts.

SUMMARY

It has been established that cesium is coprecipitated from sulfuric acid solutions together with ammonium silicomolybdate.

A technique has been developed for the flame photometric determination of microamounts of cesium in natural materials with high potassium contents.

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DETERMINATION OF THE COPPER AND MANGANESE CONTENTS OF ORES BY NEUTRON RADIOACTIVATION ANALYSIS

E. M. Lobanov, O. M. Romanov, M. M. Romanov, and
A. A. Khaidarov

Institute of Nuclear Physics, Academy of Sciences, Uzbekh SSSR, Tashkent

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The content of copper, manganese, and other elements in various samples and aluminum alloys [1-7] has been determined by neutron activation analysis. A neutron stream of $10^{12}/cm^{-2}sec^{-1}$ from a nuclear reactor was used for activating the test samples. The work described here was carried out with the aim of establishing the possibility of using γ spectrometry in activation analysis, for the determination of the copper and manganese contents of rock samples, using a stream of activating neutrons with a low intensity (10^7-10^8 neutrons/$cm^{-2}sec^{-1}$). The use of a neutron stream of such an order is of the greatest interest for the determination of the content of the elements mentioned under drilling conditions. The copper ores from deposits are mainly inclusions of chalcopyrities ($CuFeS_2$) in enclosing rocks—syenites, diorites, syenite-diorites, quartz porphyries, granodiorite porphyries. The copper content in the test rocks varies from 0.03 to 0.9%, while that of manganese (MnO) varies from 0.01 to 0.3%.

The chemical composition of a syenite-diorite is given in Table 1. The method which we have developed for the quantitative determination of Cu and Mn is based on the phenomenon of the artificial radioactivity of elements which develop on radiating them with thermal neutrons, as a result of which nonradioactive (stable) elements become radioactive. All the same, not all the elements possess an equal capacity to be activated in a neutron stream. In addition, artificially radioactive elements, in decaying, possess different half-life periods and different types of radiation, while the particles and γ quanta emitted also have different energies.

In Table 1 are given the nuclear characteristics of the elements which compose the test ore. From these results it is clear that the natural copper isotope Cu^{63} has an effective activation cross section of 3.9 b, i.e., the copper isotope indicated is readily activated by thermal neutrons. The isotope is activated according to the reaction (n, γ): $Cu^{63} + {}_0n' \rightarrow Cu^{64} + \gamma$.

The radioactive isotope Cu^{64} decays with a half life period of 12.9 hr, emitting thereby β particles and γ quanta with an energy of 0.51 mev.

Manganese has an effective activation cross-section of 12.7 b, i.e., it is very readily activated by thermal neutrons. Activation proceeds according to the reaction $Mn^{55} + {}_0n' \rightarrow Mn^{56} + \gamma$.

The radioactive isotope Mn^{56} decays with a half life period of 2.6 hr, emitting thereby β particles and γ quanta with an energy of 0.84 mev.

On the basis of the data given above, the technique for the quantitative determination of Cu and Mn in ore samples reduced to the following: samples whose percentage contents of Cu and Mn were already known were taken, they were ground, and aliquots of the samples indicated, of a definite weight (120 g), were prepared; these were the so-called standard samples. These standards were then irradiated with slow neutrons from a Po-Be neutron source, whose activity was of the order of 20 C. A paraffin block was used to slow down fast neutrons.

TABLE 1

The Nuclear Characteristics of the Elements Present in Syenite-Diorite

Chemical composition of the sample	Percentage content	Effective activation cross-section, b	Percentage content of the isotope in the natural mixture	Radioactive isotope formed	Half-life period, $T_{1/2}$	Energy of the γ radiation, mev	Yield of γ-quanta per 100 decays, %	Calculated activity I in arbitrary units for an irradiation time of 72 hr
SiO_2	60 - 30	0,12	3,08	Si^{31}	2,7 hr	1,26	0,07	2160
TiO_2	0,8—0,5	0,14	5,3	Ti^{51}	6 min	0,32	99,2	42
Al_2O_3	16—8,6	0,21	100	Al^{28}	2,3 min	1,78	100	42 000
Fe_2O_3	3,2							
FeO	3,2							
MnO	0,11—0,08	12,7	100	Mn^{56}	2,6 hr	0,84; 1,8; 2,1	99,7; 24,9; 14.8	11 430
MgO	2,2							
CaO	4—3	1,1	0,18	Ca^{49}	3,5 min	3,1; 4,05	90,10	77
Na_2O	3,5—2,6	0,54	100	Na^{24}	15 hr	1,368; 2,75; 3,86	100; 100; 0,05	20 000
K_2O	5,5—4,5	1,0	6,9	K^{42}	12,4 hr	1,51; 0,32	18,2; 0,2	2800
P_2O_5	0,3	0,23	100	P^{32}	14,3 days	—	—	—
Cu^{63}	0,5—0,35	3,9	69	Cu^{64}	12,9 hr	0,51	38	7000
	0,15	1,8	31	Cu^{66}	4,3 min	1,064	9	2700
Sr	0,001—0,001	1,3	9,8	Sr^{87}	2,7 hr	0,388	78	1
Ba	0,01—0,01	0,5	71,7	Ba^{139}	86 min	1,43; 0,63	19; 54,8	15
V	0,001—0,001	4,5	99,8	V^{52}	3,9 min	1,44	100	45 10

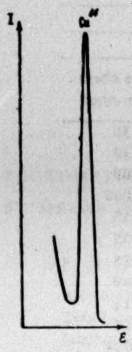

Fig. 1. Energy spectrum for the γ radiation of Cu^{64}.

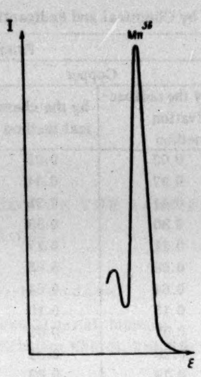

Fig. 2. Energy spectrum for the γ radiation of Mn^{56}.

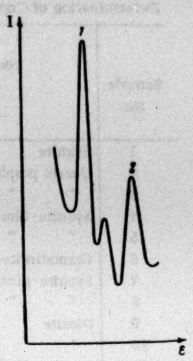

Fig. 3. Over-all energy spectrum for Cu (peak 1) and Mn (peak 2).

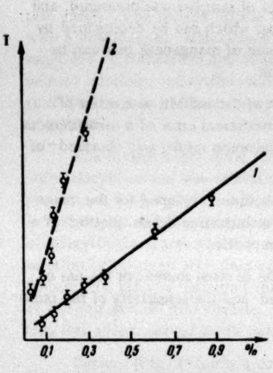

Fig. 4. Curve relating radiation intensity to Cu and Mn contents (for standard samples weighing 120 g). 1) For Cu; 2) for Mn.

The irradiation time was chosen so that a sufficiently high activity was obtained from the Cu^{64} isotope. In deciding on the irradiation time, the results of theoretical calculations of the expected activity of the various isotopes in the test sample were taken into account. Calculation of the activity of each isotope was carried out using the well-known formula [8]:

$$A = n \cdot \nu \cdot \sigma_{act.} N (1 - e^{-\lambda}).$$

where $n\nu$ is the stream of thermal neutrons, σ_{act} is the effective activation cross section of the isotopes, N is the number of isotope atoms in the sample, λ is the decay constant equal to $(0.693\ t)/T\ (^1/_2)$, and t is the irradiation time.

On the basis of the theoretical results for the activity of the various isotopes, and on the basis of the half life periods, decay curves were constructed for each isotope in order to choose the optimum measurement conditions (the time from completion of activation to the beginning of the measurements was equal to 30 min).

The γ activity of the activated samples was measured by means of a scintillation γ spectrometer [9]. The technique of measuring reduced to recording the spectra of the γ radiation of the activated sample. In Fig. 1 is shown the energy spectrum of the Cu^{64} γ radiation recorded by means of the apparatus [on this there is clearly visible a radiation maximum ("peak") corresponding to an energy of 0.51 mev for the isotope], while in Fig. 2 is shown the energy spectrum of Mn^{56} actually recorded (this has a radiation maximum with an energy of 0.84 mev).

When both Cu and Mn were simultaneously present in the sample the spectrum shown in Fig. 3 was obtained, in which peak 1 corresponds to an energy of 0.51 mev for the Cu^{64} isotope, while peak 2 corresponds to an energy of 0.84 mev for the Mn^{56} isotope. Since the peak height is proportional to the concentration of the element in the sample, this enables one to assess the concentrations of the test elements in the sample. The isotopes were identified by measuring the decrease in the intensity of the peaks on the spectra with time, in order to determine their half life period.

TABLE 2

Determination of Copper and Manganese by Chemical and Radioactivation Methods

Sample No.	Rock	Found, %			
		Copper		Manganese	
		by the radioactivation method	by the chemical method	by the radioactivation method	by the chemical method
1	Syenite	0.03	0.05	0.14	0.16
2	Quartz porphyry	0.37	0.34	0.21	0.18
3	" "	0.41	0.35	0.08	0.09
4	Syenite-diorite	0.80	0.83	0.052	0.049
5	" "	0.21	0.17	0.13	0.15
6	Granodiorite-porphyry	0.68	0.65	0.04	0.05
7	Syenite-diorite	0.64	0.64	0.06	0.03
8	" "	0.15	0.18	0.08	0.09
9	Diorite	0.07	0.09	0.11	0.13
10	"	0.28	0.31	0.16	0.14
11	Syenite-diorite	0.79	0.89	0.028	0.024
12	Diorite	0.2	0.03	0.18	0.17

In order to determine Cu and Mn quantitatively in samples, on the basis of measurements of the γ spectra of standard samples, the curve shown in Fig. 4 was constructed. Such a curve was used for determining the Cu and Mn contents of samples with unknown contents of Cu and Mn. A large number of samples was measured, and the Cu and Mn contents determined quantitatively; the minimum amount of copper which can be determined by the given method in the samples was found to be 0.03%, while the minimum amount of manganese that can be determined was found to be 0.028%, i.e., the method proved to be sensitive enough.

In Table 2 are given results for the determination of the percentage content of Cu and Mn in a series of samples, as found by our technique, and the results of a chemical method. The statistical error of a measurement did not exceed 5%. By making repeated measurements, a fairly good agreement between results was obtained – of the order of 3%.

In conclusion, it should be pointed out that further improvements in the technique developed for the quantitative determination of Cu and Mn in ores would make it possible to carry out a quantitative determination of these elements during coreless drilling of prospecting wells in the deposits in the republic.

An increase in the power of the neutron flow by increasing the activity of the neutron source, or the use of a slit neutron generator [10], would allow the duration of irradiation to be decreased and the sensitivity of the radioactivation method to be increased.

SUMMARY

The direct determination of 0.03-0.9% of Cu and 0.028-0.3% of Mn is possible with the use of a γ-ray scintillation spectrometer for recording the γ radiation of activated rock samples at a neutron flux of about 10^7 neutrons/$\mathrm{cm}^{-2} \cdot \mathrm{sec}^{-1}$. The possible experimental error is ±5-8%.

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PHOTOMETRIC DETERMINATION OF THE RARE EARTHS BY MEANS OF SALICYLFLUORONE

F. V. Zaikovskii and G. F. Sadova

All-Union Institute of Mineral Raw Material, Moscow

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The reagent arsenazo I, suggested by Kuznetsov [1], is widely used for the photometric determination of the rare earths. The present article is devoted to the description of the photometric determination of the rare earths with a new reagent—salicylfluorone [9-(o-hydroxyphenyl)-2 ,3 ,7-trihydroxyfluorone]. Salicylfluorone has been suggested by Nazarenko and Shustova [2] for the photometric determination of thorium and sulfates. In almost neutral solutions, salicylfluorone forms with the rare earths compounds with a maximum absorption at 530 mμ (just like thorium). The compounds obtained (red in color) are stabilized as a suspension in solution by means of gelatin.

The optimum pH value for obtaining the maximum color of solutions of the complexes of the rare earths with salicylfluorone was established as follows. The original weakly acid solutions (pH 3) contained 10 μg Ce_2O_3 per ml and 9 μg Y_2O_3/ml. Into 5-6 25-ml standard flasks, in one series of experiments, were introduced 30 μg lots of Ce_2O_3, and the same amount of Y_2O_3 in another series; 2 ml of a 0.2% alcoholic solution (50% ethanol) of salicylfluorone was added to each flask, followed by 0.5 ml of a 1% gelatin solution, 20 ml of an acetate buffer solution (with given pH values ranging from 3.5 to 7), and the solutions made up to the mark with water. After 30 min, the pH was measured with a potentiometer, and the optical density then measured on an FÉK-N-54 apparatus at 530 mμ in a 20 mm cuvette. Two ml of salicylfluorone solution, to which the gelatin solution and a buffer solution was added, served as the reference solution.

Cerium (Fig. 1) forms a colored compound with salicylfluorone at a higher pH than yttrium. The optical density of solutions of cerium and yttrium salicylfluoronates is most stable at pH 6.7-6.8.

In our subsequent work the buffer solution used was a 20% solution of urotropine—4 ml to 25 ml of solution (pH 6.7-6.8). A study of the solutions of the complexes formed between the metals and salicylfluorone was carried out at this pH. At higher pH values the optical density of the reagent itself increases, and this is undesirable.

The molar extinction coefficient of solutions of the salicylfluorone complexes of the rare earths was established by the "saturation" method at pH 6.8; it was found to have an average value of 17,500 for cerium, samarium, and lutecium.

The amount of salicylfluorone necessary for maximum development of the color of the cerium complex was found to be 0.75-1 ml per 25 ml of solution (Fig. 2). One ml of the 0.2% salicylfluorone solution should therefore be taken for 25 ml of test solution.

During the photometric determination of total rare earths in ores and rocks, large errors are not obtained under conditions where one or two of the elements are found in the total rare earths in predominating amounts [3]. For example, rare earth oxides of the cerium group usually contain 40% cerium and 25% lanthanum, which have atomic weights of 140.13 and 138.92, respectively; thus the "mean" atomic weight of the elements of the cerium group is close to 140. The atomic weight of the rare earths of the yttrium group "approximates" to 140; yttrium

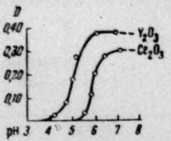

Fig. 1

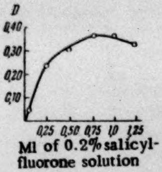

Fig. 2

with an atomic weight of 88.32, and also heavy elements with an atomic weight of 150-175. Depending on the amount of yttrium in the total rare earths, the mean atomic weight can vary by 5-10 units. Normal contents of yttrium in ores and rocks, up to 10-15%, do not appreciably change the mean atomic weight of 140.

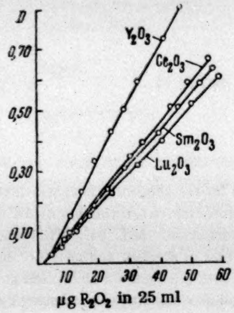

Fig. 3.

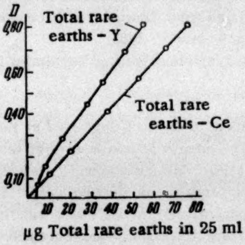

Fig. 4.

With salicylfluorone, just as with arsenazo, yttrium increases the optical density of the solution almost twice as much as cerium (Fig. 3). When yttrium predominates in the rare earths (Fig. 4), the slope of the calibration curve will also sharply differ from that of the line obtained for rare earths of the cerium group. In Fig. 4 are shown calibration curves for the cerium and yttrium groups. The composition of the main rare earth oxides (in %), as determined by the usual oxalate method in monazite, was found to be: La_2O_3 - 27.81; CeO_2 - 41.72; Pr_6O_{11} - 6.62; Nd_2O_3 - 10.6; Sm_2O_3 - 4.63; Gd_2O_3 - 3.30; and that of the yttrium group from xenothyme Y_2O_3 - 61.8; Er_2O_3 - 8.01; Lu_2O_3 - 9.8; Tb_4O_7 - 1.5; $Sm_2O_3 + Gd_2O_3$ - 6.7; Nd_2O_3 - - 8.4; Pr_6O_{11} - 2.3; CeO_2 - 2.1; La_2O_3 - 1.6. Solutions containing 10 µg total rare earths/ml (pH 3) were prepared from the rare earth oxides (by dissolving an aliquot in concentrated hydrochloric acid). With low contents of down to 10-15% of yttrium in the total rare earths, the tangents of the calibration curves for the cerium or yttrium groups do not differ sharply. Under such conditions, it is still possible to carry out photometric determinations of the total rare earths of the cerium and yttrium groups with salicylfluorone.

Sodium ethylenediaminetetraacetate, sulfosalicylic acid, etc., do not strongly affect the color of suspensions of the complexes formed between salicylfluorone and the rare earths. Calcium and magnesium form colored compounds with salicylfluorone, but they are masked by sulfosalicylic acid (0.5 ml of a 10% solution to 25 ml) and do not interfere with determination of the rare earths. This is the essential advantage of this reagent over arsenazo. It is difficult to mask calcium with sulfosalicylic acid during the reaction of the former with arsenazo [3]. Calcium always accompanies the rare earths, and, moreover, it is used as a coprecipitant in the oxalate method. Removing interference on the part of calcium often complicates analytical methods of determining the rare earths.

It is clear from Table 1 that the rare earths can be determined in the presence of large amounts of calcium (15 mg in 25 ml) with reasonable accuracy and reproducibility. Aluminum* does not form colored compounds with salicylfluorone. Tri- and divalent iron, and quadrivalent titanium, under the conditions used for determining the rare earths with salicylfluorone, form a red colored compound, solutions of which conform to Beer's law (Fig. 5). The reactions for these metals are very sensitive (0.005 µg/ml). Thorium, zirconium, and uranium form compounds with salicylfluorone; the solutions of these compounds also conform to Beer's law (Fig. 6).

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*In almost neutral solutions, aluminum reacts with arsenazo to give a colored compound.

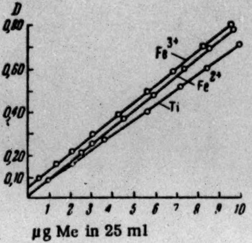

Fig. 5.

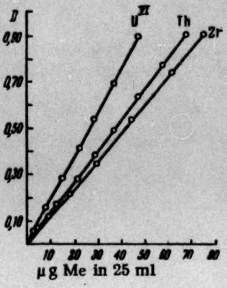

Fig. 6.

TABLE 1

Determination of Total Rare Earths in the Presence of Calcium

Taken in 25 ml		Total rare earths found, μg	Error in determination of the rare earths, μg
total rare earths, μg	Ca, mg		
10	10	9,2	−0,8
10	15	10,8	+0,8
20	10	18,1	−1,9
20	15	22,0	+2,0
50	10	52,0	+2,0
50	15	55,0	+5,0

TABLE 2

Determination of Rare Earths in Magnesium and Barium Alloys

Wt. of alloy, mg	Rare earths found, %		Error (relative), %
	by a gravimetric method	by the given method	
Ba—Ce 10,0	1,52	1,59	+4,60
Ba—Ce 20,0	0,38	0,40	+5,10
Mg—TRE* . 10,0	3,00	2,85	−5,26
Mg—Ce 20,0	1,02	0,95	−7,30

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* Total rare earths.

During determination of total rare earths in alloys (barium, magnesium alloys), separation of the rare earths from accompanying elements need not be carried out (Table 2). Barium and magnesium ions and traces of divalent iron are masked with sulfosalicylic acid, and do not interfere with determination of total rare earths. In such cases, 10-15 mg of sample is dissolved in 5-10 ml of hydrochloric acid (1 : 1), the solution is neutralized with ammonia to pH 3 using congo red paper; the solution is transferred to a 50 ml standard flask, its volume is made up to the mark with water, and the whole thoroughly mixed.

5-15 ml of the solution obtained is transferred to a 25 ml flask in order to carry out the photometric determination; to the contents of the flask are added 0.5 ml of a 1% solution of ascorbic acid, 0.5 ml of the sulfosalicylic acid solution, 1 ml of a 1% gelatin solution, 2 ml of the 0.2% alcoholic solution of salicylfluorone, and 4 ml of 20% urotropine solution, and the solution made up to the mark with water; the contents are thoroughly mixed and the optical density measured at 530 mμ in a 20 mm cuvette.

A calibration curve is constructed using the reagents indicated and a solution of the total rare earths of the cerium group containing 10-20. . . 70 μg of the rare earths in 25 ml.

It is clear from Table 2 that the rare earths can be determined in alloys by means of salicylfluorone with acceptable accuracy.

SUMMARY

Salicylfluorone forms colored compounds with the rare earths in nearly neutral solutions; solutions of these compounds conform to Beer's law. Salicylfluorone is a more selective reagent than arsenazo I. It is possible to determine certain of the rare earths and their sum photometrically by means of salicylfluorone, sulfosalicylic acid being used for masking calcium and magnesium.

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POLAROGRAPHIC DETERMINATION OF INDIUM IN METALLIC GALLIUM

S. I. Sinyakova, N. A. Rudnev, Shen Yu Ch'ih, and R. Dzhumaev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR, Moscow

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Many papers have been devoted to the polarographic determination of indium [1-6]. However, these papers are devoted either to the mechanism of the electrode reaction, or to methods for the determination of indium in the presence of other elements, in particular cadmium, at the usual indium concentrations (10^{-3}-10^{-4} M) for polarographic work. Polarographic methods have not been used for the determination of (10^{-5}-10^{-7}%) indium in high purity metals. The work described here was devoted to establishing the requisite conditions for the polarographic determination of 10^{-5}-10^{-6}% of indium, and also to methods for separating and concentrating indium during the analysis of metallic gallium.

In order to determine indium at a concentration of 10^{-6} M it was essential to choose a suitable supporting electrolyte. Very clearly defined indium waves are obtained in hydrochloric acid solutions, with $E_{1/2}$ equal to, for example in 1 M HCl, 0.60 v (relative to the saturated calomel electrode). With increasing HCl concentration, the half wave potential of indium is shifted to more negative values as a result of complex formation [7]. As our experiments showed, during polarographic examination of 10^{-6}-10^{-7} M indium solutions the HCl concentration not only affects $E_{1/2}$, but also affects the shape of the indium reduction curve, the latter being distorted at HCl concentrations greater than 2 M, while in 6 M HCl the indium wave disappears. 0.2 M HCl was accordingly chosen as the supporting electrolyte. In this region the relation between the value of the diffusion current and the indium concentration is linear over the range 2×10^{-6}- 4×10^{-5} M (Fig. 1). The limiting concentration which can be determined is 2×10^{-6} M indium.

It was also demonstrated that indium can be determined on the GEOKhI oscillograph (Model 2) [8]. In Fig. 2 are shown oscillograms for indium in 0.2 M HCl, and also the curve relating indium peak height and its concentration in solution. As is evident from Fig. 2, the curve is linear from indium concentrations within the range 1×10^{-6}- 2×10^{-5} M. The limiting indium concentration which can be determined by the oscillographic method is 5×10^{-7} M. Thus, it is possible by means of the polarographic method to determine 1×10^{-5}% of indium on a sample weight of 2 g, while by means of oscillographic polarography it is possible to determine 2.5×10^{-6}% In, for a final volume of the solution of not more than 1 ml.

In order to determine indium in gallium it is necessary to carry out a preliminary concentration of the indium.

The method which we suggest for concentrating indium is based on its coprecipitation with cobalt sulfide,* with subsequent removal of indium from gallium** and sulfate ions by extraction of indium with dithizone in the presence of sulfosalicylic acid, or by extraction of indium or gallium with diisopropyl ether.

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*Cobalt was chosen as the collector because of its very negative half wave potential.

**About 10% of gallium is coprecipitated with cobalt sulfide.

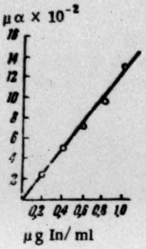

Fig. 1.

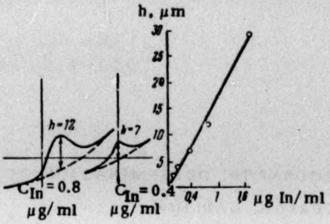

Fig. 2

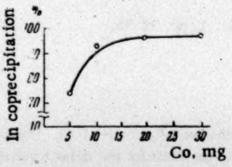

Fig. 3.

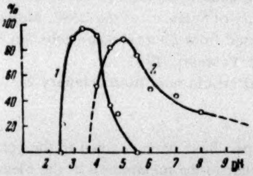

Fig. 4.

As experiments with the radioactive isotope In^{114} showed, by introducing sufficient amounts of cobalt chloride into the solution, indium is coprecipitated quantitatively with cobalt sulfide.

In Fig. 3 is shown the curve illustrating the coprecipitation of 1 μg of indium as a function of the amount of cobalt taken. For cobalt contents ranging from 15 mg upwards, the amount of indium coprecipitated amounts to 95%. In the case of 0.1 μg indium, the percentage coprecipitation is on an average 93% when 10-15 mg cobalt is used.

Of a number of masking agents for gallium (citric, tartaric, malonic acids, etc.) sulfosalicylic acid [9] proved to be the most effective at pH 4.8-5.2. This pH range proved to be the optimum for the quantitative extraction of indium as its dithizonate in the presence of sulfosalicylic acid, as is clear from Fig. 4. The maximum extraction of indium dithizonate in the presence of sulfosalicylic acid is shifted towards higher pH values than occurs with an unbuffered 10^{-3} M solution of indium [10]. It was also established by means of the radioactive isotope In^{114} that indium is quantitatively separated (even 0.1 μg In) from gallium (Ga about 0.1 g) by extracting it with diisopropyl ether from solutions containing HBr. Satisfactory separation of indium from gallium is also possible by extracting gallium with diisopropyl ether from a 6 N HCl* solution (Table 1).

As a result of the work carried out, the following method is suggested for the determination of indium in gallium. A 2-5 g aliquot of metallic gallium is dissolved on boiling in 25-30 ml aqua-regia, the latter being added in portions of about 10 ml.** The solution is evaporated to a volume of 3-5 ml, and, after cooling, 50 ml of distilled water is added. Ten-25 g of tartaric acid is added, the solution is neutralized with a 25% ammonia solution, and the pH adjusted to 7-8. Cobalt chloride solution (0.1 M) is added (1.7 ml per g of gallium***), and the indium coprecipitated with cobalt sulfide by adding 10-25 ml of 0.5 N sodium sulfide; the solution is allowed to stand for 30 min in order for the precipitate to coagulate. The sulfides are centrifuged, washed 3-4 times with a 1% solution of ammonium nitrate. The precipitate is dissolved in concentrated HNO_3 (the latter being added gradually in 3-5 ml lots) and the solution transferred to a 100 ml beaker of heat-resistant glass, in which it is evaporated to dryness. One of the following variants is then employed.

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*The indium concentration was determined polarographically.

**Dissolution proceeds slowly.

***This corresponds to 10 mg cobalt.

TABLE 1

Separation of Indium from Gallium by Extracting the Latter with Diisopropyl Ether from 6 N HCl (0.1 g gallium taken)

In added, μg	In found, μg	Error (relative) %
5.0	4.75*	−5.0
2.5	2.30*	−8.0
1.0	0.90*	−10.0

*Mean of three determinations.

TABLE 2

Determination of Indium in High Purity Gallium

In added μg	i_d, μa × $\times 10^{-2}$	In found μg	Error (relative), %
0,2	2,3	0,18	—10
0,4	4,8	0,39	−3
0,4	4,4	0,36	−10
0,6	6,3	0,51	—15
1,0	11,4	0,91	—9

The residue in the beaker is dissolved in 2-3 ml of concentrated hydrochloric acid, water is added to bring the volume up to 10 ml, 2 g of sulfosalicylic acid is added,* and the pH of the solution adjusted to 4.8–5.2.

The solution is transferred to a 50-100 ml separating funnel and the indium extracted twice with 3-5 ml of a 0.05% solution of dithizone in CCl_4. The CCl_4 layer is removed to another separating funnel, and the collected extracts washed twice with distilled water. 3-5 ml of 2 M HCl is added to decompose the indium dithizonate, the CCl_4 layer is removed and discarded, while the hydrochloric acid solution is evaporated to dryness in a small quartz basin. To the dry residue is added a few drops of concentrated $HClO_4$ and the solution evaporated to dryness on a hot plate (in order to destroy organic matter). The residue is dissolved in exactly 1 ml of 0.2 M HCl; the solution is placed in the electrolyzer and is purged with nitrogen (or hydrogen) for 5-10 min, and polarograms taken over the range 0.2 to 0.8 v at a high galvanometer sensitivity (1/2-1/3). The indium content is determined by means of a calibration curve (Fig. 1). The results given in Table 2 indicate the accuracy of the determination of indium in gallium. The relative experimental error for the determination of 0.2-1.0 μg of indium does not exceed 15%.

The solution obtained can also be analyzed by oscillographic polarography. In this case there is no need to remove the oxygen from the solution, and curves such as those shown in Fig. 2 are obtained. A calibration curve is constructed using solutions of an indium salt with a known concentration. The oscillograms of the standard and test solutions are obtained under the same operating parameters of the instrument [11].

The residue is dissolved in 2-3 ml of concentrated HNO_3, 2-3 drops of bromine is added and the solution evaporated to dryness; after cooling, 10 ml of 5 N HBr is added, and the solution evaporated to dryness. The operation of evaporation with HBr is repeated.

The dry residue is treated three times with 3-4 ml of 5 N HBr and the solutions poured into a 25 ml separating funnel. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min. After separating into two phases the aqueous layer is transferred to another 25 ml separating funnel, 10 ml of ether is added and the extraction repeated. The ethereal extracts are combined and washed twice with 5 ml of 5 N HBr. The ethereal solution is placed in a quartz crucible of about 25 ml capacity and is evaporated to dryness on a water bath. The residue is moistened with a few drops of perchloric acid, the crucible is then placed in a muffle and heated to 400-500° for 5-7 min to get a white residue.** Some more drops of perchloric acid is added and the crucible carefully heated on a hot plate until white fumes of $HClO_4$ cease to come off. After cooling, the residue is dissolved in

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*This amount of acid is sufficient to complex 0.1 g of gallium.

**If the residue is colored, this operation is repeated.

1 ml of 0.2 M HCl, the solution obtained is transferred to the electrolyzer, and the procedure outlined in the first variant then followed.

The residue is dissolved in 5 ml of 6 N hydrochloric acid and the solution transferred to a 20-25 ml separating funnel; the beaker is washed with 2-3 ml of 6 N HCl. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min; after separating into two phases, the aqueous layer is transferred to another separating funnel and the operation of extracting gallium with the ether repeated twice again, 5 ml of ether being used each time. The ethereal extracts are discarded while the hydrochloric acid solution containing the indium is evaporated to dryness in a quartz basin, the residue is then twice evaporated to dryness with a few drops of perchloric acid (to remove organic matter). The dry residue is dissolved in 0.5-1.0 ml (exactly) of 0.2 N HCl, and either polarograms or oscillograms taken, as indicated in the first variant.

Note. All the reagents should be purified beforehand. The acids and organic solvents should be distilled 2-3 times in quartz apparatus. Chemically pure grade salts should be recrystallized 2-3 times, and then additionally purified by coprecipitation with cobalt sulfide or by extraction with a solution of dithizone in CCl_4. The standard solutions of indium salts and others should be stored in quartz flasks.

The authors express their appreciation to I. P. Alimarin for his valuable assistance in conducting this work.

SUMMARY

Conditions have been developed for separating microgram amounts of indium from gallium by coprecipitating the indium with cobalt sulfide, followed by separation of indium from other components. Polarographic and oscillographic methods of determining indium in metallic gallium are suggested, which permit the determination of 10^{-5}-10^{-6}% of indium with an accuracy of ± 15%.

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POLAROGRAPHIC DETERMINATION OF NIOBIUM, TITANIUM, AND IRON IN METALLIC TANTALUM AND ITS OXIDES

D. I. Kurbatov

Institute of Chemistry, Academy of Sciences of the USSR, Ural Branch, Sverdlovsk

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The methods mainly used in analytical practice for the determination of niobium in the presence of tantalum are photometric methods which involve using the colored compounds formed with pyrogallol or thiocyanic acid [1-3]; under these conditions titanium, iron, and phosphorus interfere; the pH of the medium and the concentration of the reagents added are also of importance. Inaccurate results are obtained during the determination of titanium in the presence of considerable amounts of niobium [4]. Satisfactory results for niobium are obtained only when the optical density is measured in the ultraviolet. Spectrophotometers, however, are not available in all laboratories, and the use of ordinary colorimeters does not always give positive results.

The development of instrumental methods which could be carried out universally for the simultaneous determination of iron, titanium, and niobium without removal of tantalum is a pressing problem. Iron, titanium, and niobium are reduced in a supporting electrolyte of ortho- and pyrophosphoric acids on a dropping mercury cathode, and give well defined polarographic waves, the half-wave potentials of which are well separated from each other, and for which the limiting currents of each element are clearly defined [5-8]. The limiting currents of iron, titanium, and niobium, whether taken separately or in each other's presence, are linearly dependent on their contents in solution over a wide concentration range. These facts have been checked using comparatively large amounts of the elements listed, but the effect of tantalum (particularly at high concentrations) in solutions containing high contents of iron, titanium, and niobium has not been studied at all.

The present article is devoted to a description of a polarographic method for the determination of small amounts of iron, titanium, and niobium in metallic tantalum and its compounds.*

Pyrophosphoric acid (sp.gr. 1.9) was prepared from orthophosphoric acid (chemically pure grade) by means of a well known procedure [9]. Phosphoric acid solutions of titanium, niobium, and tantalum were prepared by fusing aliquots of their oxides with potassium bisulfate and dissolving the melt in sulfuric acid. The metal hydroxides were precipitated from this solution with ammonia, and, after their removal by filtration, were dissolved in pyrophosphoric acid (sp.gr. 1.9). Solutions were also prepared by dissolving aliquots of the oxides in hydrofluoric acid (40%), followed by removal of the hydrogen fluoride by heating the solutions with phosphoric acid until fumes of hydrogen fluoride and water ceased to be evolved.

Polarograms were taken on the SGM-8 polarograph made by the "Geologorazvedka factory." Electrolysis was carried out on a dropping mercury cathode ($m^{2}{}_{3}\ \tau^{1}/_{6} = 0.94$ mg$^{2/3}$ sec$^{1/2}$). The galvanometer sensitivity was 0.03 $\mu\alpha$ per mm of the scale. An internal mercury anode was used. The polarograms were taken at 25°.

A study of the polarographic behavior of small amounts of trivalent iron and quadrivalent titanium in the presence of tantalum was carried out in a supporting electrolyte of pyrophosphoric acid of varying concentrations. It was shown experimentally that curves with the best shape were obtained on using a ratio of $H_4P_2O_7 : H_2O = 2 : 1$ (by volume).

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*I. S. Skorynina participated in the experimental work.

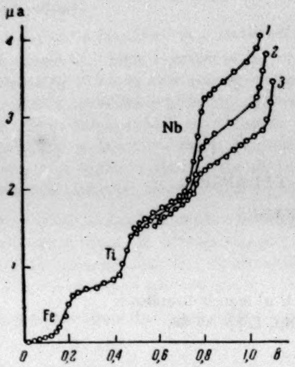

Fig. 1. Polarograms of trivalent iron. quadrivalent titanium, and quinquevalent niobium. Supporting electrolyte, pyrophosphoric acid (sp.gr. 1.85). Niobium contents: 1) 0.5%; 2) 0.25%; 3) 0.1%.

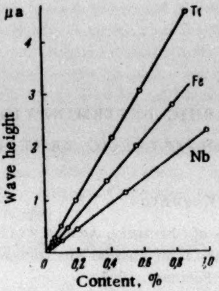

Fig. 2. The limiting current of trivalent iron, quadrivalent titanium, and quinquevalent niobium as a function of their contents in tantalum pentoxide.

Polarograms for trivalent iron and quadrivalent iron and the relationship between their limiting currents and their contents are shown in Figs. 1 and 2.

The direct proportionality between the limiting current of iron and titanium (Fig. 2, curves 1-2) against a background of considerable amounts of tantalum permits the possibility of developing a polarographic method for determining iron and titanium present as impurities in metallic tantalum and in its compounds. The advantage of the method developed is the simplicity with which it can be carried out. The method permits determination of hundredths of a percent of the elements mentioned.

Polarographic determination of niobium present as an impurity in tantalum is possible. Small amounts of niobium in the presence of tantalum give well defined polarograms with $E_{1/2} = 0.8$ v relative to the internal mercury anode, when a supporting electrolyte of pyrophosphoric acid (sp. gr. 1.9) is used (Fig. 1). The limiting current of niobium is linearly dependent on its concentration in solution (Fig. 2); tantalum ions do not exhibit any influence.

The simplicity of the method developed and its satisfactory sensitivity make it possible to recommend it for the determination of niobium in metallic tantalum and its compounds.

Determination of iron, titanium, and niobium present as impurities in metallic tantalum and its oxide. 0.5-1 g of the metal is dissolved in a platinum basin, as usual in hydrofluoric acid (40%) to which nitric acid has been added. When tantalum oxide is the test material, there is no need to add nitric acid. When the sample has dissolved completely, 20-30 ml of pyrophosphoric acid is added and the solution heated until water vapor, nitrogen oxides, and hydrogen fluoride have ceased to come off. The pyrophosphoric acid solution obtained is transferred to a standard flask (50 or 100 ml) and the volume made up to the mark with dilute pyrophosphoric acid in such an amount that its concentration in the final solution is $H_4P_2O_7 : H_2O = 2 : 1$ (by volume). An aliquot of this solution is used for the polarographic determination of iron or titanium. The electrolysis is carried out using an internal mercury anode.

For the determination of niobium, the pyrophosphoric acid solution is made up to the mark with concentrated pyrophosphoric acid (sp. gr. 1.85-1.9), the solution obtained is carefully mixed and is then used for taking polarograms. Electrolysis is carried out using an internal mercury anode.

It was pointed out above that on a dropping mercury cathode, trivalent iron is first reduced; this is followed by quadrivalent titanium, and finally niobium (Fig. 2). The tantalum present in solution does not affect the diffusion current of the elements being reduced.

Polarographic Determination of Niobium, Titanium, and Iron Present as Impurities in Metallic Tantalum and its Oxide

Nb found, %		Ti found, %		Fe found, %	
by a chemical method [3]	by the polarographic method	by spectrographic method	by polarographic method	by a spectrographic method	by the polarographic method
1.04	1.05	0 33	0.03	0.22	0.21
	1.07		0.03		0.20
	1.04		0.03		0.22
12.8	12.7	0.99	0.98	1.48	1.50
	12.8		0.99		1.49
	12.7		0.97		1.48

Accordingly, favorable conditions are created for the simultaneous determination of iron, titanium, and niobium on one polarogram. In this case, the sample must be prepared in the same way as that indicated for the determination of niobium. During the successive determination of iron, titanium, and niobium, when pyrophosphoric acid (sp.gr. 1.9) is used as the supporting electrolyte, the diffusion rate decreases because of the increasing concentration of the supporting electrolyte; consequently, the diffusion current of iron and titanium falls somewhat. Nevertheless, the sensitivity of the method can be increased by increasing the weight of sample taken, and by using a more sensitive apparatus, e.g., a differential or an oscillographic polarograph.

As is evident from the table the method gives satisfactory results during the simultaneous determination of the elements mentioned in the presence of tantalum.

SUMMARY

Small amounts of iron, titanium, and niobium (0.01-1.0%) give clearly defined polarograms in the presence of a large amount of tantalum (99%) when pyrophosphoric acid is used as the supporting electrolyte; the limiting currents are proportional to the concentration of the elements. A method has been developed for the determination of the metals mentioned, when they are present as impurities in metallic tantalum and its oxide, using only one polarogram; the relative experimental error is ± 3-5%.

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COMPOUNDS OF MOLYBDENUM WITH THIOGLYCOLIC ACID AND A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF MOLYBDENUM

A. I. Busev and Chang Fang

M. V. Lomonosov Moscow State University

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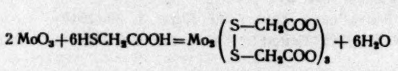
Thioglycolic acid gives with molybdate a color [1] which is used for its detection [2, 3] and for its photometric determination [4-6]. Ziegler, et al. [7] have noted that the compound formed between molybdenum and thioglycolic acid can be extracted with organic solvents in the presence of tri-n-butylammonium salts. Recently, extraction [8] and chromatographic methods [9] have been suggested for separating molybdenum from vanadium by means of thioglycolic acid.

Richter [4] found, using a photometric method, that sexivalent molybdenum interacts with thioglycolic acid in the molar ratio of 1 : 3. The reaction proceeds according to the following suggested equation:

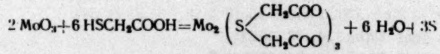
$$MoO_3 + 3\,HSCH_2COOH = Mo\,(SCH_2COO)_3 + 3H_2O.$$

Richter is of the opinion that the colored compound formed is a simple salt of trivalent molybdenum with dithioglycolic acid, although this suggestion is not reflected in the formula $Mo(SCH_2COO)_3$. According to Richter, dithioglycolic acid is formed during the oxidation of thioglycolic acid by sexivalent molybdenum. Meyer [10] has advanced the hypothesis, on the basis of Richter's experimental results [4] regarding the molar ratio, that sexivalent molybdenum reacts with thioglycolic acid according to one of the following equations, or according to both simultaneously:



$$2\,MoO_3 + 6HSCH_2COOH = Mo_2\left(\begin{matrix} S\text{—}CH_2COO \\ | \\ S\text{—}CH_2COO \end{matrix}\right)_3 + 6H_2O$$

A salt of dithioglycolic acid



$$2\,MoO_3 + 6\,HSCH_2COOH = Mo_2\left(S\begin{matrix} \diagup CH_2COO \\ \diagdown CH_2COO \end{matrix}\right)_3 + 6\,H_2O + 3S$$

A salt of thiodiglycolic acid

Meyer [10] considers that molybdenum is trivalent in these compounds. There is no direct evidence at all in the articles of Richter [4] and Meyer [10] for the reduction of sexivalent molybdenum to the trivalent state. Thioglycolic acid, although it does possess reducing properties, is still not strong enough for one to expect it to reduce sexivalent molybdenum to the trivalent state. It is, apparently, capable under certain conditions of reducing molybdenum to the quinquevalent state only. Such an assumption is confirmed by the fact that thioglycolic acid has been successfully used as a reducing agent for sexivalent molybdenum during its detection by the thiocyanate method [11]. Will and Yoe [5] have pointed out that on increasing the thioglycolic acid concentration (> 0.4% by volume) during the photometric determination of molybdenum, the optical density decreases, probably, as they suggest, as a result of the partial reduction of sexivalent molybdenum by excess reagent with the formation of a colorless complex. Thus a literature review shows that the position with regard to the valence of molybdenum in the compounds formed is not clear; consequently, the composition of these compounds is uncertain,

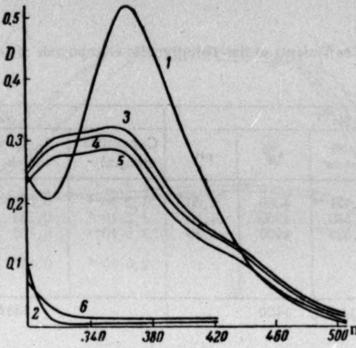


Fig. 1. Absorption curves of solutions of the compounds of thioglycolic acid with sexi- and quinquevalent molybdenum at various pH's. 1) The compound of sexivalent molybdenum, pH 4; 2) thioglycolic acid; 3) the compound of quinquevalent molybdenum, pH 1.78; 4) the compound of quinquevalent molybdenum obtained by mixing solutions of molybdate with thioglycolic acid and adjusting the pH to 0.52; 5) the compound of quinquevalent molybdenum, pH 0.55; 6) dithiodiglycolic acid.

and so is the mechanism of the interaction of molybdate with thioglycolic acid. We set outselves the problem of filling this essential gap in the literature.

EXPERIMENTAL METHOD

The concentration of the aqueous sodium molybdate solution used was established by the 8-hydroxyquinoline method [12]. One ml was found to contain on an average 4.99 mg Mo.

A solution of quinquevalent molybdenum was prepared by reducing a standard hydrochloric acid solution of sodium molybdate with metallic mercury [13], or with hydrazine hydrochloride [14]. In both cases the hydrochloric acid concentration of the final solution was 1 M. Results obtained with both solutions of the quinquevalent molybdenum salt almost coincided.

The trivalent molybdenum salt $(NH_4)_2MoCl_5$ was prepared as described earlier [15].

The concentration of aqueous solutions of a commercial preparation of thioglycolic acid was established iodometrically [16] at various acidities of the solution. The molar concentration of the thioglycolic acid solution was found to be: 0.2061 M (pH 3), 0.02067 M (2 M HCl), 0.02071 (0.4 M HCl) and 0.02055 M (0.04 M HCl), giving a mean value of 0.020603 M.

The optical density was measured on a SF-4 spectrophotometer using a layer thickness of 1 cm. The pH of the solution was measured by a LP-5 pH-meter using a glass electrode.

The valence of molybdenum in the yellow colored compounds formed with thioglycolic acid. Our experiments showed that thioglycolic acid and also dithiodiglycolic acid do not interact with trivalent molybdenum [in the form $(NH_4)_2MoCl_5$] at pH 1-4 to form a yellow colored compound. The assumptions of Richter [4] and Meyer [10] are therefore not confirmed experimentally.

Thioglycolic acid interacts with quinquevalent molybdenum [in the form $(NH_4)_2MoCl_5$] at various pH values (from 1 to 6). During this reaction a stable yellow color develops which is somewhat less intense than that which a solution of ammonium molybdate of the same molarity gives. The assumption of Will and Yoe [5] that quinquevalent molybdenum gives a colorless complex with thioglycolic acid is not confirmed experimentally either.

TABLE 1

Molar Extinction Coefficients of the Thioglycolic Compounds of Sexi- and Quinquevalent Molybdenum

Mo^{VI}				Mo^{V}			
Concentration, M	$D^{365}_{l=1\ \text{см}}$	ε^{365}_{M}	pH	Concentration, M	$D^{365}_{l=1\ \text{см}}$	ε^{365}_{M}	pH
$4 \cdot 10^{-5}$	0,171	4300	4,00	$1,2 \cdot 10^{-4}$	0,296	2500	0,84
$1,2 \cdot 10^{-4}$	0,530	4400	4,20	$1,2 \cdot 10^{-4}$	0,283	2400	0,55
$1,2 \cdot 10^{-4}$	0,525	4400	4,80	$2,0 \cdot 10^{-4}$	0,465	2300	0,3*M* HCl
				$2,0 \cdot 10^{-4}$	0,467	2300	0,3*M* HCl
	Mean:	4400			Mean:	2400	

Dithiodiglycolic acid (taken in excess) does not give colored compounds with either quinque- or sexivalent molybdenum for pH values of 1-4 and 1-7, respectively.

It should be pointed out that the compounds of quinquevalent and sexivalent molybdenum with thioglycolic acid differ not only in the intensity of their colors, but also with respect to some other properties.

In a comparatively acid medium (pH < 3) the compound of sexivalent molybdenum with thioglycolic acid is reduced by excess of the latter to the quinquevalent molybdenum compound. On adding alkali to the compound of quinquevalent molybdenum with thioglycolic acid, the yellow color of the compound changes to the red color of an unstable compound, which rapidly breaks down; under these conditions quinquevalent molybdenum is oxidized to the sexivalent state; on subsequent acidification to pH 3-6 of the solution obtained, there appears the yellow color of a compound of sexivalent molybdenum, when the solution contains excess thioglycolic acid.

It is interesting to note that when excess thioglycolic acid is present during the reduction of sexivalent molybdenum or the oxidation of quinquevalent molybdenum in a weakly acid medium, formation of molybdenum blue is not observed.

Formation of a yellow compound of sexivalent molybdenum with thioglycolic acid is also confirmed by the following experiments. To 2 ml of 0.02 M sodium molybdate solution at pH 1-3 is added 1.0 ml of a very dilute (0.002 M) thioglycolic acid solution, with stirring. The thioglycolic acid is added in a known, lower molar amount with respect to the molybdenum. A distinct yellow color immediately appears. However, after a few minutes, the solution becomes blue because of the formation of molybdenum blue, in which some of the molybdenum is known to be in the quinquevalent state, while some is present in the sexivalent state. When a relatively large excess of thioglycolic acid is used, formation of molybdenum blue is not observed.

Photometric characteristics of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid. The absorption curves of solutions of the compounds of thioglycolic acid with sexi- and quinquevalent molybdenum at various pH values are given in Fig. 1. The solutions were prepared as follows: in a 25 ml standard flask was placed 1.5 ml of a 2×10^{-3} M solution of sodium molybdate or of a quinquevalent molybdenum salt (in 1 N HCl) and a weakly acid (pH 4-5) solution of thioglycolic acid added in such amount that, after dilution, its concentration was 0.4% by volume. The pH of the solution was carefully adjusted by addition of dilute sodium hydroxide or hydrochloric acid solutions, dropwise, with careful stirring. It is necessary to avoid local increases in acid or alkali concentration as much as possible. Only by observing this precaution is it possible to avoid premature, partial reduction of sexivalent molybdenum and oxidation of quinquevalent molybdenum. After this stage the solution was diluted to the mark and its pH measured with a glass electrode. The optical density was measured on a SF-4 spectrophotometer using a cuvette with a layer thickness of 1 cm; the reference solution was a solution prepared in the same way, but omitting molybdenum.

Solutions of the sexivalent molybdenum compound at pH 4 have a maximum absorption at 365 mμ (Fig. 1). The absorption curve of solutions of the compound of sexivalent molybdenum with thioglycolic acid differs from the absorption curve of the compound of quinquevalent molybdenum with thioglycolic acid at pH 4. Solutions

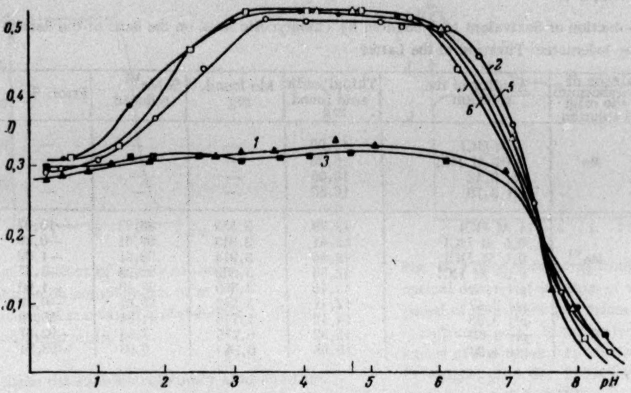


Fig. 2. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid and pH. The final concentrations of sexi and quinquevalent molybdenum were the same and equal to 1.2×10^{-4} M; the thioglycolic acid concentration was constant and equal to 0.4% by volume. 1) Mo^{V} + + $HSCH_2COOH$ at different pH values; 2) Mo^{V} + excess $HSCH_2COOH$; the pH was adjusted to 10 or higher; after 15 min HCl was added to adjust the pH to varying values; 3) Mo^{V} + + excess $HSCH_2COOH$ + HCl until the concentration was 0.5 M; NaOH was added after 15 min to bring the pH to varying values; 4) Mo^{VI} in the presence of excess $HSCH_2COOH$; the solution in Expt. No. 3 was adjusted to pH > 10; after a few minutes HCl was added to bring the pH to varying values; 5) Mo^{VI} + excess $HSCH_2COOH$ (pH of the mixture 4.2), and NaOH added to adjust the pH to varying values; 6) Mo^{VI} + excess $HSCH_2COOH$; NaOH was added to bring the pH > 10; HCl was finally added (after a few minutes) to bring the pH to varying values.

of the quinquevalent molybdenum compound at pH 0.55 and 1.78 have one absorption maximum at 352.5 mμ (Fig. 1). The absorption curves obtained by mixing ammonium molybdate and thioglycolic acid at pH 0.52 and by mixing the compound of quinquevalent molybdenum almost coincide with one another. In both cases the absorption maximum lies at 352.5 mμ. This shows that at pH 0.52 sexivalent molybdenum is reduced by thioglycolic acid to the quinquevalent state; the latter forms a yellow colored compound with excess reagent.

Dithiodiglycolic acid $HOOCCH_2-S-S-CH_2COOH$, which is formed during the reduction of sexivalent molybdenum, does not affect the absorption of the solutions obtained in the operative wavelengths. It starts to absorb light appreciably at wavelengths below 320 mμ (Fig. 1). The dithiodiglycolic acid solution used for obtaining the absorption curve was prepared by oxidizing 1.5 ml of 0.02 M thioglycolic acid with iodine, removing excess of the latter by reduction with $Na_2S_2O_3$, and diluting with water to 25 ml.

The molar extinction coefficient of the thioglycolic compound of sexivalent molybdenum at 365 mμ and at the optimum pH was found to be 4400, while that of the thioglycolic compound of quinquevalent molybdenum was found to be 2400 (Table 1).

Conditions under which compounds of sexi- and quinquevalent molybdenum with thioglycolic acid exist. Of the greatest interest is the establishment of the conditions for reduction of sexivalent molybdenum with thioglycolic acid and establishing the acidity range within which the respective compounds of sexi- and quinquevalent molybdenum exist. In order to get comparable results, the final concentration of sodium molybdate and of the quinquevalent molybdenum salt in all cases was the same (1.2×10^{-4} M), while the thioglycolic acid concentration was always 0.4% by volume. The pH of the solution was adjusted to the requisite value very carefully, as was done during obtaining the absorption

TABLE 2

Reduction of Sexivalent Molybdenum by Thioglycolic Acid on the Basis of the Results of the Iodometric Titration of the Latter

Valence of molybdenum in the original solution	Acidity of the solution	Thioglycolic acid found, mg	Mo found, mg	% Mo^{VI} reduced	Error, %
Mo^{V}	1 *M* HCl	16,09	—	—	—
	0,04 *M* HCl	16,26	—	—	—
	pH 2,42	16,05	—	—	—
	pH 3,78	16,59	—	—	—
Mo^{VI}	1 *M* HCl	12,79	3,559	89,93	—10,07
	0,5 *M* HCl	12,41	3,943	99,61	—0,39
	0,1 *M* HCl	12,44	3,914	98,91	—1,09
	0,05 *M* HCl	12,54	3,809	96,23	—3,77
	pH 1,82	12,45	3,895	98,40	—1,60
	pH 2,47	12,41	3,943	99,61	—0,39
	pH 3,03	14,49	1,775	44,84	—55,16
	pH 3,63	15,92	0,278	7,03	—92,97
	pH 3,98	15,96	0,240	6,06	—93,94

curves. The optical density was measured at 365 mμ relative to water. For solutions with pH 3, the optical density was measured half an hour after preparing them, when the optical density had become constant. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid (when excess of the latter was present) and the pH of the solutions is shown in Fig. 2. Comparison of Curves 1-6 in Fig. 2 makes it possible to come to a final decision in regard to acidity limits within which compounds of quinque- and sexivalent molybdenum with thioglycolic acid exist, and to solve the question of the conditions under which these compounds mutually change into each other. The thioglycolic compound of quinquevalent molybdenum is formed within a wide acidity range of the solution ranging from 0.5 M HCl to pH 6 (Fig. 2, Curve 1). Under these conditions, the optical density of the solutions is almost independent of the acidity of the solution. On increasing the pH from 6 to 8, a rapid decrease in the intensity of the yellow color occurs.

On increasing the pH of solutions of the compound of quinquevalent molybdenum with thioglycolic acid to pH 10 and above (in the presence of excess thioglycolic acid),* oxidation of quinquevalent molybdenum by atmospheric oxygen or by hydrogen ions occurs. When the solution obtained under these conditions is carefully acidified with hydrochloric acid until the solution is weakly acid (pH 3.5-6), a yellow color appears. The molar extinction coefficient is 4200. The absorption curve of this solution almost coincides with the absorption curve of the compound of sexivalent molybdenum with thioglycolic acid of equal molar concentration. This fact confirms that quinquevalent molybdenum is oxidized to the sexivalent state under the experimental conditions. The compound of sexivalent molybdenum with thioglycolic acid is stable at pH 2.5-6. At pH < 3 sexivalent molybdenum is reduced with thioglycolic acid to the quinquevalent state. Under these conditions the molar extinction coefficient decreases from 4300 to 2500, i.e., to a value which is characteristic for the quinquevalent molybdenum compound.

By altering the pH of solutions containing excess thioglycolic acid, it is possible to convert molybdenum almost quantitatively from the sexivalent state to the quinquevalent state, and the quinquevalent to the sexivalent state. This is confirmed by the agreement found between the values for the molar extinction coefficients for the respective solutions and those found earlier for the sexi- and quinquevalent molybdenum compounds.

The fact that sexivalent molybdenum is reduced quantitatively to the quinquevalent state by excess thioglycolic acid in an acid medium is also confirmed by its iodometric titration. Quinquevalent molybdenum under certain conditions is not oxidized by iodine, and does not appreciably affect the titration of thioglycolic acid (Table 2). To a molybdate solution of known concentration was added excess of a standard solution of thioglycolic acid, which was first neutralized with alkali to a pH of 4-5; the acidity of the solution was adjusted to a definite value, and the solution diluted to 25 ml with water saturated with CO_2; the solution was left for about three hours and the thioglycolic acid solution titrated with iodine solution (0.01 N) using starch as indicator. Near the end point the yellow color of the molybdenum compound was observed to disappear gradually; accordingly, it was

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*Thioglycolic acid in excess prevents the hydrolysis of quinquevalent molybdenum. The solution remains clear throughout the whole pH range.

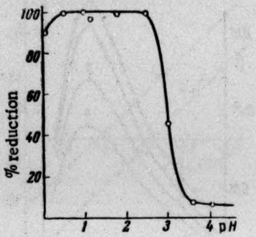

Fig. 3. Effect of acidity of the solution on completeness of reduction of sexivalent molybdenum with thioglycolic acid.

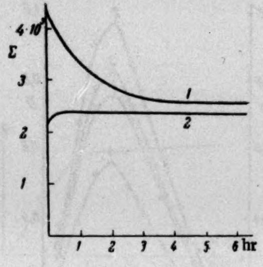

Fig. 4. Effect of standing time on the optical density of solutions of the compound of sexivalent molybdenum with thioglycolic acid, in the presence of excess of the latter. 1) 2% $HSCH_2COOH$ by weight, pH 4.48; 2) 0.4% $HSCH_2COOH$ by volume in 0.3 M HCl.

necessary to shake the solution vigorously after addition of each drop of iodine solution, the drops being added at intervals. Titration was complete when there was a distinct change to blue on addition of a drop of iodine, this color being stable for several minutes. The amount of molybdenum was calculated on the assumption that it was reduced from sexivalent to the quinquevalent state. The results are given in Table 2 and in Fig. 3. From Fig. 3 it is clear that at pH < 2.5 sexivalent molybdenum is completely reduced to the quinquevalent state. Excess reagent forms a colored compound with quinquevalent molybdenum. Our results have justified the use of thioglycolic acid [11] for reducing sexivalent molybdenum during its detection by the thiocyanate method.

In 1 M HCl low results are obtained, probably because of the partial oxidation of quinquevalent molybdenum by iodine at such an acidity. At pH 2.5-3.5, sexivalent molybdenum is incompletely reduced by thioglycolic acid. In a weakly acid medium (pH > 3.5), probably, reduction of molybdenum only proceeds to a negligible amount, and is dependent on the excess concentration of thioglycolic acid. There is a published reference [5] to the fact that at high thioglycolic acid concentrations (> 0.4%), the yellow color arising from the molybdenum complex at pH 4 gradually decreases, and the hypothesis is advanced that the reason for this may be partial reduction of molybdenum by excess reagent with formation of a colorless compound. In our experiments, at high thioglycolic acid concentrations (2% by weight) and at pH 4.48, the optical density, measured relative to water at 365 mμ, gradually changes on standing; this shows that reduction of sexivalent molybdenum under the conditions indicated, proceeds slowly; nevertheless, after four hours, almost all the molybdenum is found in the quinquevalent state. Under these conditions $\varepsilon^{365}_{M} = 2600$ (Fig. 4). After 24 hr the yellow color of the solution has changed to brown, probably as the result of sulfide formation.

In principle it should be possible to determine sexivalent molybdenum by iodometric titration of excess thioglycolic acid.

On the basis of our results it is obvious that at pH 3.5-6 thioglycolic compounds of sexivalent and quinquevalent molybdenum with an intense yellow color exist. At pH > 6, both compounds decompose, the quinquevalent molybdenum changing into the sexivalent stage. At pH < 2.5, only the thioglycolic acid compound of quinquevalent molybdenum is stable. Under such conditions, sexivalent molybdenum changes quantitatively into the quinquevalent state in the presence of excess thioglycolic acid.

The composition of the compounds formed by the interaction of thioglycolic acid with sexi- and quinquevalent molybdenum. The ratio between sexivalent or quinquevalent molybdenum and thioglycolic acid in the colored compounds formed was established by the isomolar series method. Varying volumes of 0.2063 M solutions of sodium molybdate or quinquevalent molybdenum salt (in 1 M HCl) were mixed with an almost neutral 0.02063 M solution of thioglycolic acid so that the sum of the molar concentrations of both components was always constant and equal to 9.90×10^{-4} M. The acidity of the solutions was adjusted by means of a buffer solution with pH 3.6, or by the careful addition of the calculated amount of hydrochloric acid. The optical density was measured

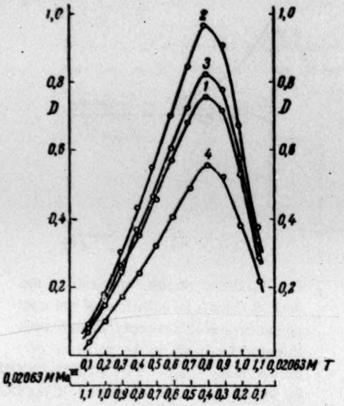

Fig. 5. Interaction of sexivalent molybdenum with thioglycolic acid at pH 3.6. The optical density was measured relative to water. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

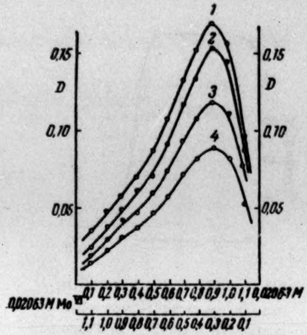

Fig. 6. Interaction of sexivalent molybdenum with thioglycolic acid in 0.02 M HCl. The optical density was measured relative to water. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

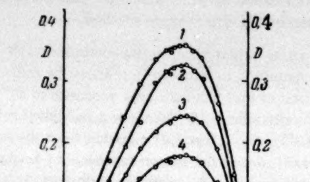

Fig. 7. Interaction of quinquevalent molybdenum with thioglycolic acid in 0.02 M HCl. The optical density was measured relative to solutions of a quinquevalent molybdenum salt of equal concentration in 0.02 M HCl. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

at 345, 365, 385, and 405 mμ. Two series of solutions were prepared in the case of sexivalent molybdenum. In one series the solutions had a pH of 3.6; under these conditions the reaction is instantaneous; the optical density was measured not later than 30 min after mixing; on standing for a longer time some of the solutions become blue. The other series of solutions, which had a constant hydrochloric acid concentration (0.02 M HCl), was allowed to stand for two hours before measuring the optical density in order for the reduction of molybdenum to reach equilibrium. In the experiments with quinquevalent molybdenum, a series of solutions with a final hydrochloric acid concentration of 0.02 M was prepared (taking into account the hydrochloric acid in the original solution). The results obtained are given in Figs. 5-7.

From Fig. 5 it is clear that the maximum optical density (for solutions at pH 3.6) is observed at a molar ratio of Mo^{VI} to thioglycolic acid of 1 : 2. This allows one to write the following equation for the reaction:

$$MoO_2^{2+} + 2HSCH_2COOH = MoO_2\ (SCH_2COOH)_2 + 2H^+ \quad (1)$$

The maximum optical density in the case of sexivalent molybdenum in 0.02 M HCl is observed at a molar ratio of molybdenum to thioglycolic acid of 1 : 3, i.e., three moles of thioglycolic acid correspond to one mole of molybdate (Fig. 6). Richter [4] obtained the same molar ratio by adding increasing amounts of thioglycolic acid to a molybdate solution (10 mg Mo^{VI}), and measuring the optical density of the neutral solutions which he says he obtained (presumably, the solutions in his experiments were weakly acid). In attempting to repeat Richter's experiments [4] we obtained poorly reproducible and often idefinite results.

Quinquevalent molybdenum interacts with thioglycolic acid in a molar ratio of 1 : 2 (Fig. 7).

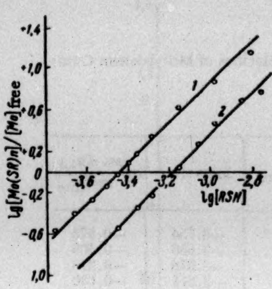

Fig. 8. The relation between $\log([Mo(SR)_n]/[Mo]_{free}$ and $\log[RSH]_{free}$ for solutions of molybdenum compounds with thioglycolic acid. 1) Sexivalent molybdenum; 2) quinquevalent molybdenum.

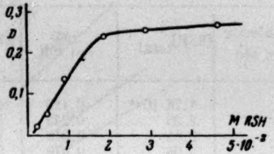

Fig. 9. The effect of thioglycolic acid concentration on the optical density of the solutions. Concentration 1.2×10^{-4} M Mo, 0.3 M HCl; 365 mμ.

By comparing the results obtained it is possible to assume that during the interaction of sexivalent molybdenum in 0.02 M HCl, one mole of thioglycolic acid is used in reducing the molybdate to quinquevalent molybdenum, and then two moles of thioglycolic acid interact with one mole of quinquevalent molybdenum. Thus, it can be regarded as established that in acid solutions the reaction proceeds as follows:

$$2\,MoO_2^{2+} + 6\,HSCH_2COOH = Mo_2O_3(SCH_2COOH)_4 + HOOCCH_2S{-}SCH_2COOH + 4H^+ + H_2O \qquad (2)$$

The molar ratios at which quinque- and sexivalent molybdenum react with thioglycolic acid were also determined by the slope of the lines. The original solutions contained 2.0×10^{-4} M of sexivalent molybdenum and 4.0×10^{-4} M of quinquevalent molybdenum. The optical density was measured at 365 mμ, at which wavelength solutions of quinquevalent and sexivalent molybdenum hardly absorb at all. The optical density of the sexivalent molybdenum solutions was measured as soon as possible after they had been prepared, so that no molybdenum blue was formed in the presence of excess molybdate. Solutions of quinquevalent molybdenum were allowed to stand for two hours in order to attain a constant optical density. The final sexivalent molybdenum solutions had a pH of 3.6. The hydrochloric acid concentration of the final quinquevalent molybdenum solutions was 0.02 M.

When the line slope method was used it was assumed that the reaction proceeds as follows:

$$Mo^{VI,V} + n\,RSH = Mo(SR)_n + nH^+.$$

$$K_{eq} = \frac{[Mo(SR)_n] \cdot [H^+]^n}{[Mo^{VI,V}]_{free}\,[RSH]^n_{free}}.$$

Since the experiments were carried out in solutions with constant acidity, then on taking logarithms of the expression, we get for the constants:

$$n \lg [RSH]_{free} = \lg \frac{[Mo(SR)_n]}{[Mo]_{free}} + \text{const}.$$

When the values of $\log \dfrac{[Mo(SR)_n]}{[Mo]_{free}}$ are plotted along the ordinate, while the values of $\log [RSH]_{free}$ are plotted on the abscissa, then a straight line is observed. The slope (tangent α) of the straight line will be numerically

TABLE 3

Relation Between log $\frac{[Mo(SR)_n]}{[Mo]_{free}}$ and log $[RSH]_{free}$ for Solutions of Molybdenum Compounds with Thioglycolic Acid

Valence of Mo	$[RSH]_{total}$	D^{365} $l=1$ cm	$[Mo(SR)_n]$	$[Mo]_{free}$	log[RSH]	$\log\frac{[Mo(SR)_n]}{[Mo]_{free}}$
Mo^{VI}	$1,76\cdot10^{-4}$	0,185	$4,2\cdot10^{-5}$	$15,8\cdot10^{-5}$	—3,754	—0,575
	2,20	0,245	5,6	14,4	—3,658	—0,409
	2,64	0,310	7,0	13,0	—3,578	—0,268
	3,08	0,370	8,4	11,6	—3,511	—0,140
	3,52	0,425	9,7	10,3	—3,454	—0,025
	3,96	0,480	11,0	9,0	—3,402	+0,086
	4,40	0,523	11,9	8,1	—3,357	+0,167
	5,28	0,603	13,7	6,3	—3,277	+0,336
	7,04	0,710	16,1	3,9	—3,152	+0,616
	10,56	0,776	17,6	2,4	—2,976	+0,866
	15,84	0,810	18,4	1,6	—2,800	+1,125
Mo^{V}	$3,52\cdot10^{-4}$	0,215	$0,89\cdot10^{-5}$	$3,10\cdot10^{-4}$	—3,454	—0,538
	4,40	0,295	1,23	2,77	—3,356	—0,347
	5,28	0,360	1,50	2,50	—3,277	—0,222
	7,04	0,500	2,08	1,90	—3,152	+0,033
	8,80	0,620	2,58	1,42	—3,055	+0,260
	10,56	0,710	2,96	1,04	—2,976	+0,455
	14,48	0,790	3,30	0,70	—2,839	+0,674
	17,60	0,820	3,42	0,58	—2,754	+0,771

TABLE 4

Determination of Molybdenum in the Presence of Foreign Elements

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error
0,1 Cr $(Cr(NO_3)_3\cdot9H_2O$	0,60	0,62	+0,02	2,4 Total rare earths oxides	0,38	0,37	—0,01
1,0 Cr $(Cr(NO_3)_3\cdot9H_2O$	0,60	0,60	0				
1,5 Cr $(Cr(NO_3)_3\cdot9H_2O$	0,38	0,37	—0,01	29,5 Total rare earths oxides	0,38	0,38	0
10,4 Cr $(Cr(NO_3)_3\cdot9H_2O$	0,38	0,39	+0,01				
0,5 V (V_2O_5)	0,60	0,60	0	400,0 Thiourea	0,38	0,39	+0,01
1,0 V (V_2O_5)	0,60	0,60	0	1,3 Cu$(CuSO_4\cdot5H_2O)$*	0,38	0,38	0
1,7 V (V_2O_5)	0,38	0,41	+0,03	8,4 Cu$(CuSO_4\cdot5H_2O)$*	0,38	0,38	0
2,2 Ti $(Ti(SO_4)_2)$	0,38	0,38	0	11,2 Fe$(FeCl_3\cdot6H_2O)$**	0,38	0,38	0
18,5 Ti $(Ti(SO_4)_2)$	0,38	0,37	—0,01	3,0 W$(Na_2WO_4\cdot2H_2O)$***	0,47	0,47	0

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*In the presence of 0.5 g thiourea.

**In the presence of 0.2 g ascorbic acid.

*** After filtering off turbidity of $WO_3\cdot nH_2O$.

equal to n. The results obtained are given in Table 3. From Fig. 8, the slope of line 1 is 1.94, while that of line 2 is 2.0. Accordingly, both quinque- and sexivalent molybdenum interact with thioglycolic acid in molar ratios of 1 : 2 at pH 3.6.

These results coincide with the results obtained by the isomolar series method.

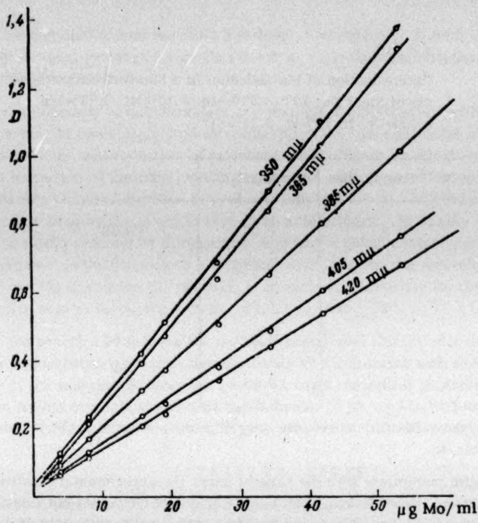

Fig. 10. Calibration curves.

Colored compounds of sexi- and quinquevalent molybdenum with thioglycolic acid (at an acidity corresponding to pH 5.1 and 0.1 M HCl) migrate to the anode, i.e., molybdenum is found in the form of anionic complex compounds.

Sexi- and quinquevalent molybdenum interact with thioglicolic acid, apparently via the sulfhydryl group, not through the carboxyl group.

An improved version of the photometric determination of molybdenum with thioglycolic acid. As already explained, when a large excess of thioglycolic acid is present in moderately acid solutions, the thioglycolic acid completely reduces molybdate to quinquevalent molybdenum, which then interacts with excess reagent to give a fairly intense yellow color. Within the acidity limits pH 2.5 to 0.5 M HCl, the optical density of the solutions obtained is almost constant, while most of the accompanying elements do not form colored compounds with thioglycolic acid under these conditions. In this way it is possible to increase the selectivity of the determination of molybdenum with thioglycolic acid. At a thioglycolic concentration of 2.5×10^{-2} M, the optical density of 1.2×10^{-4} M solutions of molybdenum reaches a maximum value and remains almost constant on increasing its concentration further (Fig. 9). The optical density becomes constant 15 min after preparing the solutions, and does not change in the course of several hours (Fig. 4).

Calibration curve. Ten ml of a standard solution of sodium molybdate containing not more than 1 mg of molybdenum is introduced into a 25 ml flask; 1.3 ml of dilute hydrochloric acid (1 : 1) is added; in this case the HCl concentration in the final solution will be 0.3 M. Two ml of 0.5 M thioglycolic acid solution is then added, and the solution diluted to the mark with water; the whole is thoroughly mixed and the solution allowed to stand for 20 min; the optical density is measured at 365 mμ or 350 mμ with respect to water. The solutions conform to Beer's law (Fig. 10) at 350, 365, 385, 405, and 420 mμ. The method permits determination of molybdate at concentrations ranging from 1 to 40 μg per ml.

Determination of molybdenum in the presence of foreign elements. We have studied the possibility of determining molybdenum in the presence of those elements which interfere with its determination in variants of the thioglycolate method suggested earlier [5]. Experiments with synthetic mixtures were carried out in the same way

TABLE 5

Determination of Molybdenum in a Standard Sample of Steel No. 197 (0.97% Mo, 0.10% Ni, 0.29% Mn, 0.32% Cr, 15.72% W, 0.31% Si)

Sample No.	Mo found, %	Error, %
1	0.99	+0.02
	0.98	+0.01
2	0.97	0
	0.92	−0.05
3	0.97	0

as that used for constructing the calibration curve, the only difference being that the solution was first neutralized. The results are given in Table 4.

Copper gives a yellowish precipitate with the reagent under the experimental conditions and interferes with molybdenum determination. Nevertheless, even large amounts of copper do not interfere, if it is complexed with thiourea. Large amounts of trivalent iron do not interfere with the determination if it is first reduced to the divalent state with ascorbic acid (under these conditions, the molybdate is also reduced to the quinquevalent state); accordingly there is no need to remove molybdenum from iron during the determination of molybdenum in steel. Tungstate does not give a color with the reagent, but at 0.3 M HCl it separates out as a precipitate or in the form of a suspension. The precipitated tungstic acid strongly affects the optical density; accordingly, it must be filtered off through filter paper. When large amounts of tungstate are present, high results are obtained for molybdenum if the solution is allowed to stand for a long time. Quadrivalent vanadium is masked by sodium fluoride at pH 2, and a colorless solution is obtained. Univalent mercury gives a black precipitate with the reagent and interferes with the determination. Large amounts of chromium, titanium, and rare earths do not interfere with molybdenum determination. Compared with the method in which molybdenum is determined at pH 3-5 by means of thioglycolic acid, the method which we recommend has a higher selectivity, does not necessitate separation of molybdenum from iron, and ensures that a color which is stable with time is obtained; this method, however, is less sensitive.

Determination of molybdenum in steel. A sample of steel weighing about 0.25 g is placed in a 100 ml beaker and is dissolved in a mixture of 5 ml HNO_3(1 : 1) and 5 ml H_2SO_4 (1 : 1); the solution is evaporated to the appearance of white H_2SO_4 fumes. If the steel does not dissolve completely, a few ml of HCl (1 : 1) is added and the solution evaporated to dryness; this operation is repeated several times until the steel has dissolved. After cooling, 20 ml of water is added and the solution heated to dissolve the salts. Insoluble silicic acid is filtered off on a filter paper, the filter paper plus precipitate are washed several times with the minimum amount of water, and the filtrate collected in a 50 ml standard flask. After cooling, the solution is diluted to the mark with water, and a suitable aliquot of this solution pipetted into a 25 ml flask. Ascorbic acid (0.2 g per 10 mg iron) is added, and, after a few minutes, most of the acid is neutralized with alkali (to pH 2-3 according to universal indicator paper). The procedure subsequently followed is the same as that used for constructing the calibration line. When the steel contains tungsten, the tungstic acid which separates out must be removed by filtration.

Satisfactory results have been obtained during the determination of molybdenum in a standard sample of steel No. 197 (Table 5).

SUMMARY

Under certain conditions, molybdenum, both in the quinque- and sexivalent state, forms a yellow colored compound with thioglycolic acid. Maximum absorption is observed at 352.5 and 365 mμ, respectively, while

the respective molar extinction coefficients are 2400 and 4400. Molybdenum in both valence states interacts with thioglycolic acid (R) in equal molar ratios of Mo : R = 1:2. Trivalent molybdenum does not give a yellow colored compound with thioglycolic acid.

The stability of the compounds of quinquevalent and sexivalent molybdenum with thioglycolic acid depends on the acidity of the solution. In moderately acid solutions (pH < 2.5) the compound of sexivalent molybdenum with thioglycolic acid is unstable, and reduction of sexivalent molybdenum by thioglycolic acid to the quinquevalent state occurs, with formation of the corresponding compound with excess thioglycolic acid. The compound of quinquevalent molybdenum obtained is stable in acid solutions (pH 0.7-6). Molybdenum is only completely reduced to the quinquevalent state by thioglycolic acid in an acid solution. In weakly acid media (pH 2.5-6) sexivalent molybdenum is slowly reduced by thioglycolic acid to the quinquevalent state, only in the presence of a very large excess of reagent. In the absence of a large excess of reagent, the sexivalent molybdenum compound is fairly stable at pH 2.5-6. On increasing the pH there is an increased tendency for the quinquevalent molybdenum compound with thioglycolic acid to be oxidized to the sexivalent state.

The selectivity of the reaction of quinquevalent molybdenum with thioglycolic acid in a weakly acid medium (in 0.3 M HCl) is considerably higher than the selectivity of the reaction with sexivalent molybdenum at pH 3-5. The sensitivity of the reaction is, however, lower. A highly selective photometric method has been developed for the determination of small amounts of molybdenum (1-40 μg Mo/ml) in alloyed steels. Vanadium and large amounts of titanium, the rare earths, iron, copper, and tungsten do not interfere.

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COMPLEXONOMETRIC TITRATION OF QUADRIVALENT URANIUM USING THORON AS INDICATOR

P. N. Palei and Hsu Li-Yan

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR, Moscow

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The stability of the complex compound of uranyl with sodium ethylenediaminetetraacetate (EDTA-Na) is low. EDTA-Na is used mainly as a masking agent during the separation of uranium from many elements by precipitation [1-3], extraction [4-7], and chromatography [8, 9], and also during the determination of uranium gravimetrically [3, 10-14], photometrically [15-18], and polarographically [19]. The uranyl ion forms a stable compound with EDTA-Na at pH 3.5-4.0. In contrast to other metals which react with EDTA-Na in the proportion of 1 : 1, in the given instance two atoms of uranyl correspond to one molecule of the EDTA [20-21].

In pure solutions, UO_2^{2+} ions can be determined by high frequency complexonometric titration [20]. Takomoto [22] has tried to determine uranyl ions by back titration in an acetate buffer solution by means of the salt of divalent cobalt and potassium thiocyanate, but he did not obtain satisfactory results. Lassner and Scharf [23] have suggested a rapid method for titrating uranyl ions at pH 4.4-4.6 with EDTA-Na solution, using 1-(2-pyridylazo)-2-naphthol as indicator; titration is carried out in a 1 : 2 mixture of water and isopropanol.

Quadrivalent uranium forms a very stable, soluble, complex compound with EDTA-Na, and uranium is not precipitated from solutions of this compound by means of ammonia. This fact has been used for separating quadrivalent uranium from titanium and beryllium [24]. The complexonometric method of determining quadrivalent uranium is based on boiling a solution of uranyl acetate with excess EDTA-Na at pH 3-4 in the presence of ascorbic acid, which acts as a reducing agent, and titrating excess EDTA-Na with thorium nitrate solution in the presence of xylenol orange at pH 2-3 [25].

The aim of the work described here was to find a suitable indicator for the complexonometric titration of quadrivalent uranium.

Alizarin red S gives a red color with quadrivalent uranium in acid media [26]. We tried to use it as an indicator for the complexonometric titration of quadrivalent uranium, but it was found that the red color disappears too soon—before the equivalence point is reached.

Pyrocatechol violet (pyrocatechol sulfophthalein) forms colored complex compounds with tri- and quadrivalent cations in acid media, while it only forms colored complex compounds with divalent metals in alkaline media. Pyrocatechol violet has been successfully used for the complexonometric determination of thorium [27, 28] and bismuth [29, 30]. Quadrivalent uranium forms a red compound with pyrocatechol violet at $pH < 1.8$, while at $pH > 1.8$ a violet colored compound is formed. We have used pyrocatechol violet as an indicator at pH 1.0-2.0, but we found that the color changes before the equivalence point.

Thoron (benzene-2-arsonic acid-<-1-azo-1->-2-hydroxy-naphthalene-3,6-disulfonic acid) forms a rose colored compound with quadrivalent uranium [31]; it has been used for the photometric determination of uranium [32, 5]. The stability constant of this compound is equal to $9.2 \pm 0.5 \times 10^9$ [32]. Thoron is used as an indicator during the complexonometric determination of bismuth at pH 1.3 [33].

TABLE 1

Determination of Uranium with Thoron as Indicator at pH 1.5

U^{IV} taken, mg	Amount of EDTA-Na solution used, ml	U^{IV} found, mg	Error		Notes
			mg	%	
9,85	4,60	9,86	+0,01	0,1	Titration with 0.0090 *M* EDTA-Na solution
19,70	9,17	19,66	—0,04	0,2	
29,55	4,56	29,50	—0,05	0,2	» 0,0270 *M* The same
39,40	6,10	39,20	—0,02	0,5	
50,20	4,67	50,35	+0,15	0,3	» 0,0453 *M* » »
5,02	7,76	4,99	—0,03	0,6	» 0,0027 *M* » »
3,01	4,67	3,00	—0,01	0,3	
2,01	3,15	2,00	+0,01	0,5	
1,00	1,55	1,00	±0	0	
0,50	7,78	0,50	±0	0	» 0,00027 *M* » »
0,30	4,69	0,30	±0	0	
0,20	3,04	0,195	—0,005	2	
0,10	1,60	0,103	+0,003	3	

TABLE 2

Effect of Acidity on Titration when Thoron is Used as Indicator

U^{IV} taken, mg	Amt. of 0.0027 M EDTA-Na solution used, ml	pH	U^{IV} found, mg	Error	
				mg	%
5,02	7,72	1,0	4,98	—0,04	0,8
3,01	4,68	1,0	3,01	+0	0
2,01	3,11	1,0	2,00	—0,01	0,5
1,00	1,54	1,0	0,99	—0,01	1,0
5,02	7,08	2,0	4,55	—0,47	9
2,01	2,85	2,0	1,83	—0,19	9
5,02	7,76	1,8	4,99	—0,03	0,6
3,01	4,67	1,8	3,00	—0,01	0,3
1,00	1,55	1,8	0,996	—0,004	0,4
5,02	7,76	0,8	4,99	—0,03	0,6
3,01	4,70	0,8	3,02	+0,01	0,3
2,01	3,10	0,8	1,994	—0,016	0,8
2,01	—	0,5			
1,00	—	0,5			

In the work described here we studied the requisite conditions for the use of thoron as an indicator during the complexonometric titration of quadrivalent uranium.

Quadrivalent uranium was prepared by reducing uranyl on a mercury cathode in dilute perchloric acid.

As is evident from Table 1, amounts of uranium from 0.1 to 50 mg are titrated satisfactorily at pH 1.5. At uranium concentrations greater than 0.5 mg/ml of solution, the solution acquires a green-brown color, as a result of which it is difficult to detect the titration end point. It was found that a distinct color change could be obtained at the end point by adding 6-10 drops of a 0.1% solution of indicator while warming the solution (30°).

During a study of the effect of acidity on the titration of quadrivalent uranium, the pH was measured on completion of titration with a glass electrode using an LP-5 potentiometer. Good results are obtained at pH 1.0-1.8 (Table 2). Increasing the pH to 2.0 causes the color change to occur before the titration end point. On dropping the pH to 0.8 the color change becomes indistinct, while at pH 0.5 the rose color hardly changes at all even on adding a considerable excess of EDTA-Na; this is explained by the fact that in more acid media the compound of quadrivalent uranium with EDTA-Na is less stable than that with thoron.

It is clear from Table 3 that the alkali and alkaline earth elements, zinc, divalent manganese, aluminum, lead, lanthanum, and cadmium do not interfere with the titration.

Thorium and bismuth interfere with the titration, since, under the given conditions, they react with EDTA-Na and form rose colored compounds with thoron.

Zirconium also forms a rose colored compound with thoron, and a precipitate is formed on adding a solution of a zirconium salt to the solution being titrated; a similar phenomenon is observed during the photometric titration of zirconium with thoron [34].

Quadrivalent titanium decreases the distinctness of the color change at the end point, since it reacts with thoron to form a rose-orange colored compound. Trivalent titanium, as a strong reducing agent, destroys the indicator and the solution becomes colorless.

TABLE 3

Effect of Various Elements on the Titration of Quadrivalent Uranium with EDTA-Na Using Thoron as Indicator at pH 1.5

U^{IV} taken, mg	Foreign ions taken, mg	0.0090 M EDTA-Na used, ml	U^{IV} found, mg	Error	
				mg	%
10,04	Al 200	4,60*	10,08	+0,04	0,4
9,85	Th 5	6,58	14,11	+4,26	43,0
9,85	La 5	4,61	9,88	+0,03	0,3
9,85	Cd 5	4,58	9,82	−0,03	0,3
9,85	Zn 5	4,60	9,86	+0,01	0,1
9,85	Ce^{4+} 5	4,91	10,53	+0,70	7,0
10,04	Ce^{3+} 2,5	4,68	10,04	±0	0
10,04	Mn^{2+} 20	4,68	10,04	±0	0
10,04	Mg 100	4,67	10,02	−0,02	0,2
10,04	Ca 100	4,68	10,04	±0	0
9,85	Cr^{3+} 5	4,61	9,88	+0,03	0,1
10,04	Ti^{IV} 5	1,56**	10,03	−0,01	0,1
9,85	Fe^{2+} 5	4,60	9,86	+0,01	0,1
10,04	Fe^{2+} 50	4,61*	10,10	+0,06	0,6
10,04	Fe^{3+} 100	5,27*	11,54	+1,50	15
9,85	Co 5	4,71*	30,27	+20,42	200
9,85	Ni 5	1,76**	11,31	+1,46	15
10,04	Ni 2,5	4,68	10,04	±0	0
9.85	Cu 5	4,03**	25,90	+16,05	160
10,04	Bi 5	3,22**	20,70	+10,66	100
10,04	Hg^{2+} 5	3,13**	20,11	+10,07	100
10,04	Pb 20	4,69	10,06	+0,02	0,2
10,04	V 1,0	3,84	8,23	−1,81	18
10,04	AsO_4^{3-} 2,5	2,78	10,25	+0,21	2,0
10,04	AsO_4^{3-} 1,0	4,68	10,04	+0	0
10,04	CH_3COO^- 1 *M* 2 ml	4,69	10,06	+0,02	0,2
10,04	F^- 1	4,04	8,66	−1,38	14
10,04	NaCl 2 g	4,59*	10,05	+0,01	0,1
10,04	$NaNO_3$ 2 g	4,60*	10,08	+0,04	0,4
10,04	Na_2SO_4 2 g	4,62*	10,12	+0,08	0,8
10,04	Na_2SO_4 1 g	4,60*	10,08	+0,04	0,4

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*Titration carried out with 0.0092 M EDTA-Na solution.

**Titration carried out with 0.0270 M EDTA-Na solution.

Cobalt, copper, and mercury interfere most strongly, since they also react with EDTA-Na. Vanadium interferes with the titration, since it is reduced during electrolysis to the divalent state, and destroys thoron.

Trivalent cerium, nickel up to 2.5 mg, and divalent iron up to 50 mg do not affect the titration.

Trivalent chromium forms a very stable compound with EDTA-Na [35], but since the reaction between them proceeds slowly, chromium does not interfere with the titration.

Divalent tin interferes since it is hydrolyzed to give a precipitate which adsorbs the indicator. In the presence of molybdate and tungstate blue and yellow precipitates similar to the compound of thorium with molybdenum separate out [36]. Arsenate interferes with the titration even at low concentrations (1 mg); it is very difficult to detect the titration end point in this case.

Nitrate, chloride, and acetate do not interfere with the titration. When sulfate is present the color change is indistinct, particularly at low uranium concentrations. Fluoride interferes fairly strongly, but interference on its part can be eliminated by adding an aluminum salt.

As a result of the experiments we have carried out the following method has been developed for the determination of uranium.

TABLE 4

Masking of Fluoride Ions by Means of Aluminum during the Complexonometric Titration of Quadrivalent Uranium Using Thoron as Indicator (10.04 mg U taken)

0.0092 M EDTA-Na solution used, ml	Fluoride ion added, mg	Aluminum added, mg	U^{IV} found, mg	Error	
				mg	%
4,58	5	100	10,03	—0,01	0,1
4,59	5	100	10,05	+0,01	0,1
4,59	20	200	10,05	+0,01	0,1
4,60	20	200	10,08	+0,04	0,4
4,59	30	200	10,05	+0,01	0,1
4,61	30	200	10,10	+0,06	0,6
4,61	50	200	10,10	+0,06	0,6
4,63	50	200	10,14	+0,10	1,0

TABLE 5

Determination of Uranium in its Tetrafluoride Using Thoron as Indicator

U^{IV} taken, mg	EDTA-Na solution used, ml	U^{IV} found, mg	Error		Notes
			mg	%	
Perchloric acid medium					
19,98	9,12	19,97	—0,01	0,05	Titration with 0.0092 M EDTA-Na solution
19,98	9,14	20,01	+0,03	0,15	
9,99	4,55	9,96	—0,03	0,3	
9,99	4,57	10,01	+0,02	0,2	
9,99	4,56	9,99	±0	0	
5,00	9,21	4,98	—0,02	0,4	" 0.00226 M "
5,00	9,23	4,99	—0,01	0,2	
4,00	7,38	3,99	—0,01	0,2	
4,00	7,41	4,00	±0	0	
2,00	3,73	2,01	+0,01	0,5	
2,00	3,69	1,99	—0,01	0,5	
2,00	3,70	2,00	±0	0	
Hydrochloric acid medium					
18,65	8,52	18,65	±0	0	Titration with 0.0092 M EDTA-Na solution
18,65	8,51	18,64	—0,01	0,05	
9,32	4,26	9,33	+0,01	0,1	
9,32	4,25	9,31	—0,01	0,1	
4,66	8,63	4,66	±0	0	" 0.00227 M "
4,66	8,63	4,66	±0	0	
3,73	6,88	3,72	—0,01	0,3	
3,73	6,88	3,72	—0,01	0,3	
1,86	3,45	1,86	±0	0	
1,86	3,42	1,85	—0,01	0,5	
1,86	3,46	1,87	+0,01	0,5	

Ten ml of uranyl chlorate in 1 N perchloric acid is reduced electrolytically on a mercury cathode; the solution obtained after electrolysis is transferred to a 50 ml standard flask and diluted with water to the mark. Five ml of this solution is pipetted from the flask, 3 ml of 1 N perchloric acid is added and the volume diluted to 100 ml with water. After adding 6-10 drops of a 0.1% solution of the thoron indicator, the solution acquires a rose color. The quadrivalent uranium is then titrated with EDTA-Na solution (it is best to heat the solution to 30° prior to titration). At the end point the color of the solution changes from rose to orange-yellow.

The method developed has been used for determining uranium in its tetrafluoride.

Uranium tetrafluoride was prepared by precipitation from aqueous solutions according to a published method ([26], p. 30). The precipitate obtained was dried in a desiccator over $CaCl_2$ to constant weight. The quadrivalent uranium content was controlled by titration with ammonium vanadate [37].

Quadrivalent uranium can be determined by direct complexonometric titration using thoron as indicator at pH 1.0-1.8 (Table 2). As is evident from Table 4, fluoride is well masked by aluminum; it is only at a ratio of uranium to fluoride of 1 : 5 that the end point is indistinct, but such a ratio is not often met in practice.

For the determination of uranium in its tetrafluoride, an aliquot (0.2 g) of the latter is dissolved in 10 ml of 1 N perchloric or hydrochloric acid in which 1 g of $AlCl_3 \cdot 6H_2O$ has been dissolved beforehand. After the aliquot has dissolved, the solution is transferred to a 50 ml standard flask and diluted with water to the mark. A known volume of this solution is pipetted from the flask and 3 ml of 1 N perchloric or hydrochloric acid added; the solution is then diluted with water to 100 ml; 6-10 drops of the 0.1% solution of thoron is added and the uranium titrated with 0.01 M or 0.003 M EDTA-Na solution until the color of the solution changes from rose to orange-yellow.

As is evident from Table 5, results for the determination of uranium in its tetrafluoride are completely satisfactory.

SUMMARY

It has been established that it is possible to titrate quadrivalent uranium complexonometrically with thoron as indicator at pH 1.0-1.8; the titration can be carried out in the presence of a number of elements. A method is suggested for the determination of quadrivalent uranium in its tetrafluoride, using aluminum ions for masking the fluoride.

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SPECTROGRAPHIC DETERMINATION OF TRACES OF BERYLLIUM IN URANIUM

P. N. Palei and E. V. Bezrogova

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There are three groups of methods for the determination of microamounts of Be [1]: photometric [2-6], fluorescent [2,5], and spectrographic [1, 7]. The first two groups require that Be be removed beforehand from interfering elements. In some cases, in the presence of sodium ethylenediaminetetraacetate (EDTA-Na), it is possible to determine Be directly; uranium, however, forms an unstable complex [8] and will interfere with the determination [9, 10]. Moreover, the sensitivity of these methods (approximately 10^{-4}%) is too low. A published spectrographic method [7] permits determination of beryllium in uranium without preliminary separation, but the sensitivity of this method (10^{-3} and 10^{-4}%) is also too low.

Our problem was to develop a method for determining 10^{-6}% Be in uranium. Several methods are known for separating beryllium and uranium: chromatographic separation of Be, U, and Ti on paper [11], a similar separation using complexons [8, 12], electrochromatographic separation on paper [13], and chromatographic separation on a cation exchange resin using various complexing agents [14-17].

The latter technique would appear to be the most promising for separating small amounts of beryllium from large amounts of uranium.

Experimental part. The test material chosen was a metal sample containing almost 100% of uranium. It was checked spectrographically for its Be content (Be < 0.0001%); from this sample a solution of UO_2Cl_2 was prepared containing 39 g uranium/liter. Aliquots of this solution were taken for the experiments.

The beryllium solution (0.2 μg/ml) was prepared by dissolving beryllium oxide, chemically pure grade, in hydrochloric acid, evaporating this solution almost to dryness, and then diluting. All the remaining solutions of salts, acids, and alkalis were prepared from chemically pure grade materials.

The particle size of the cation exchange resins KU-2 and SBS which were used was 1 to 0.25 mm; they were given a preliminary treatment to free them from impurities, and were converted into the H-form.

First of all we tried to absorb beryllium alone by means of a cation exchange resin (KU-2 or SBS), leaving the uranyl in solution (pH 3-5) in the form of its oxalate complex. Experiments showed that only 40-50% of the beryllium is sorbed on the resin, the remainder staying in the filtrate with the uranyl. Presumably at high oxalate concentrations, beryllium may be partially complexed.

Separation of beryllium and uranium on a cation exchange resin in the form of their sulfosalicylate complexes. Beryllium is capable of forming a relatively stable complex with sulfosalicylic acid at pH 3-4; UO_2^{2+} ions also give a complex, but at pH $\geq$ 4.4.

Beryllium and uranium were sorbed together on KU-2 cation exchange resin; the beryllium was then eluted separately with sulfosalicylic acid at a definite pH value; under these conditions the uranyl ion was not eluted.

The optimum separating conditions are as follows: 1) separation is completely satisfactory when the particles of the KU-2 resin have a diameter of 0.25 mm. Reduction of the particle size further slows down the process; 2) the optimum elution rate proved to be 0.5 ml/min; under these conditions there is no rapid superposition of

TABLE 1

Taken		Amt. of eluate, ml	Be found, µg		%, extracted
U, mg	Be, µg		in the eluate	in the regenerate	
450	200	700	185	–	92.5
450	200	700	205	–	102.5
450	100	700	100	–	100.0
450	50	800	Not determined	0.45	99.0
450	50	700	"	1.5	97.0

one zone by another; 3) an important factor is the amount of resin, which, in turn, depends on the aliquot taken and determines the distance between the zones of the elements being eluted (on issuing from the column). It was established that in a column with a diameter of 10 mm, and when a 1 g aliquot is taken, it is necessary to have a minimum of 10 g KU-2 resin in the air dry state; 4) one of the chief factors which determine the separation is the acidity of the eluting solution. The best separation is obtained at pH 3; variations can only be permitted toward lower pH values; at pH > 3 superposition of zones occurs, and uranium starts to come off with the beryllium.

The separation consists of the following: a hydrochloric acid solution (0.6 M HCl) containing uranium and beryllium is passed through a column of KU-2 resin in the H-form at a rate of 0.5 ml/min. Uranium and beryllium are sorbed on the resin. The sorbent is next washed with 50 ml of distilled water. The beryllium is eluted with a 0.025 M sulfosalicylic acid solution with a pH of 3 (adjusted by means of ammonia). During the passage of the eluent, there is observed the formation of a dark violet ring right at the top of the column which gradually proceeds downward; this is determined by the presence of traces of iron. Elution of beryllium occurs simultaneously with that of the sulfosalicylate complex of iron, since a beryllium ring is not detected in the eluate prior to elution. When no iron is present (no ring is observed), elution of the beryllium can be observed by following the change in the pH of the eluate; beryllium starts to come off at pH 2.7-3 and its elution is complete either after elution of all the ring or after the appearance of the reddish color of the uranyl complex with sulfosalicylic acid. The eluate collected prior to the elution of the ring (or up to pH 2.7-3) is rejected, and the second portion of eluate (400-500 ml) is taken for analysis. This eluate is evaporated almost to dryness (in a platinum basin), concentrated sulfuric acid is added, and excess of the latter removed by evaporation. The residue obtained is calcined at 300-400° to burn off carbon; it is then fused with $KHSO_4$ in order to convert the BeO into a soluble state and the melt dissolved in a known volume of water. Depending on the expected amount of beryllium either all the solution or an aliquot of it is taken for analysis. Beryllium is determined by the normal fluorescent method. When the sample taken contains some uranium, after calcining to obtain U_3O_8 the residue is weighed and a spectrographic finish used.

Uranium is desorbed with 2 N HCl, the uranium in the eluate is precipitated with ammonia, and the precipitate obtained is calcined and analyzed spectrographically. The possibility of effecting complete separation was checked using solutions of uranium containing from 10^{-2}-10^{-3}% beryllium. Fully satisfactory results were obtained (Table 1).

In order to check the method at lower beryllium contents (10^{-4}-10^{-6}%), a uranium preparation was used which had been specially purified from beryllium by sorption on KU-2 resin and elution with sulfosalicylic acid.

For determining beryllium in such amounts, it is necessary not only to separate it from uranium, but also to concentrate it in such a way that the beryllium can be determined by the usual methods (fluorescent, spectrographic, etc.). The experimental technique was the same; only the amounts of uranium and accordingly the column dimensions were altered. Two series of experiments were carried out using a spectrographic and a fluorescent finish, respectively.

TABLE 2

Taken		Amt. of eluate, ml		Amt. of precipitate as U, mg	Be obtained µg	% Extracted
U, g	Be, mg	Be	Be+U			
Be alone eluted (20 mg U added)						
1,5	0,05	510	—	25,4	0,025	50
1,5	0,05	430	—	26,2	0,026	48
Be + U eluted (up to 30 mg uranium)						
1,5	0,05	460	25	27,1	0,03	60
1,5	0,05	370	25	28,4	0,03	60
Be + U eluted (above 30 mg uranium)						
1,2	0,1	325	35	33,1	0,08	80
1,6	0,05	200	30	44,7	0,05	100
1,5	0,05	460	35	38,6	0,06	120
1,5	0,05	220	35	39,9	0,04	80

1) Fluorescent determination. Experiments showed that for contents of 1-0.1 µg of Be in 1 g of U, only 50% of the beryllium is eluted from the resin in 100-200 ml of eluate, and a large amount of eluate is required to eluate it completely. Since on passing further amounts of sulfosalicylic acid solution through the column uranium starts to emerge, the fluorescent method is inapplicable; only a spectrographic finish is possible.

2) Spectrographic determination. Elution of Be and U with sulfosalicylic acid was carried out as follows: a) elution was only carried out to the appearance of the color of the uranium complex with sulfosalicylic acid (only Be eluted); in this case, 20 mg of the original uranium (free from beryllium) was added to a sample of eluate, and the residue analyzed spectrographically; b) the beryllium was eluted to a stage at which some of the uranium had come through. Observations were based on the color of the uranium complex; for elution of 20-40 mg of uranium, it was found sufficient to collect 25-40 ml of eluate with the clearly marked color of the uranium complex. The residue, after decomposing the complexes and calcining to U_3O_8, was analyzed spectrographically. The results are given in Table 2.

Accordingly, in order to obtain satisfactory results, it is necessary to elute 35-40 mg of uranium together with the beryllium. This suggests that the partition zones of Be and U even on the resin are, presumably, superimposed on each other, this being particularly the case during elution of traces of Be (down to 10^{-6}%).

Technique for determining traces of Be in uranium. A known amount of uranium, the amount depending on the expected beryllium content (1.5-2 g of uranium for a Be content down to 10^{-6}%), is dissolved in hydrochloric acid to which hydrogen peroxide has been added; the solution is evaporated almost to dryness and then diluted with water to 100 ml. The solution is acidified to 0.6 M with respect to HCl and is passed through a column 10 mm in diameter containing KU-2 resin in the H-form (15-20 g of resin in the air dry form for 1.5-2 g uranium). The rate at which the solution is passed through the column is 0.5 ml/min. The resin is then washed with 50 ml of water and the Be eluted with sulfosalicylic acid (0.02-0.025 M) at a pH of 2.7-3. During this stage a clearly defined dark violet zone is observed which gradually passes down the column; the eluate prior to the elution of this ring, or before the eluate has a pH of 2.7-3, is discarded, and the following portion of eluate taken for analysis. Elution is complete when 35-40 ml of solution with the distinct color of the complex of uranium with sulfosalicylic acid has been collected (total volume of eluate 400-500 ml). The eluate is evaporated almost to dryness, 3-5 ml of concentrated H_2SO_4 is added to destroy the complexes and the residue is calcined, initially at 300-400° to burn off carbon, and then at 800-850° to obtain U_3O_8. The residue is weighed and the Be determined spectrographically. One determination takes about 40 hr.

SUMMARY

A combined method is suggested for the determination of down to 10^{-6}% of beryllium in uranium; the beryllium is concentrated chromatographically and then determined spectrographically. The experimental error is ± 20%.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION II. PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF URANIUM BY MEANS OF BROMOPYROGALLOL RED*

V. F. Luk'yanov and E. P. Duderova

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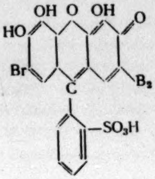
Bromopyrogallol red has been suggested as a complexonometric indicator for the determination of a number of elements [1]:



The reagent, which belongs to the sulfophthalein group of indicators, gives red solutions in acid media, and violet or blue colored solutions in neutral and alkaline media. It forms blue or blue-violet colored complexes with the following metal ions, at various pH values: Bi, Pb, Hg, Cu, Cd, Sb, Sn, Fe, Al, Ni, Co, Zn, Mn, Ca, Sr, Ba, Mg, rare earths, U, Th, Ti, Zr.

We have used bromopyrogallol red as a reagent for the uranyl ion. In the course of our work we established that the compound formed is stable at pH 5-7. A urotropine buffer solution with pH 6.5-7 was used to maintain the necessary pH. In this medium the reagent has a red color, while its complex with uranium has a blue-violet color.

The absorption curves of the reagent and the complex are shown in Fig. 1, while the calibration curve is shown in Fig. 2.

It is clear from Fig. 1 that the most suitable wavelength for the work is 620 mμ, at which the difference between the optical densities of the complex and the reagent is a maximum.

The complex is formed almost instantaneously, and its color is very stable (for at least 24 hr).

The maximum optical density of the solutions, obtained by the Ostromyslenskii-Job method, is observed at a ratio of UO_2^{2+} : reagent = 1 : 1 (at 600, 620 and 630 mμ) for three different initial molar concentrations of uranium salt and reagent (0.9×10^{-4} M; 1.8×10^{-4} M; and 3.6×10^{-4} M).

The molar extinction coefficient of solutions of the compound at 620 mμ is 8.8×10^3 (mean of three determinations).

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*For Communication I, see Zhur. Anal. Khim. 15, 184 (1960).

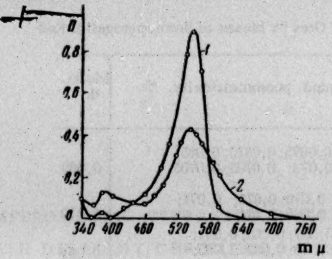

Fig. 1. Light absorption of solutions of the complex of uranium with bromopyrogallol red, and of the reagent (SF-4, cuvette 1 cm). 1) 2×10^{-5} M solution of pyrogallol red; 2) solution of the complex of uranium with bromopyrogallol red at a ratio of UO_2^{2+} : reagent = 1 : 1.

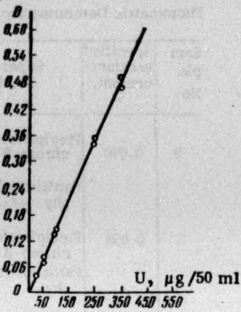

Fig. 2. Calibration for the determination of uranium with pyrogallol red (FÉK-M, red filter, cuvette 3 cm).

When an FÉK-M photocolorimeter is used, uranium can be reliably determined at a minimum concentration of 0.5 μg/ml (red filter, cuvette 3 cm, D = 0.04).

The most suitable concentration range for the photometric determination of uranium is 25 to 250 μg uranium in 50 ml; Beer's law is observed over this range.

Quantitative determination of uranium requires preliminary separation from accompanying elements, most of which form compounds with bromopyrogallol red [1]. We decided on a method developed by V. I. Titov, A. A. Lavrova, and E. P. Osiko in 1956. This method is based on separating uranium with α-nitroso-β-naphthol as a coprecipitant, in the presence of sodium ethylene diaminetetraacetate (EDTA-Na). When this separation method is used, appreciable amounts of iron and traces of certain other metals are precipitated together with the uranium. We used EDTA-Na for eliminating interference from iron; the former was added (in slight excess) until no color of iron thiocyanate was detected.

Analytical procedure. One-half to 1 g of test material (depending on the uranium content) is decomposed with hydrochloric acid containing hydrogen peroxide by heating on a sand bath. The solution is diluted with water and the insoluble residue filtered off and washed. To the filtrate, whose volume should be about 100 ml, is added 15-17 ml of a 10% solution of EDTA-Na; the pH is adjusted to 7.5-8 using neutral red (or universal indicator), and the solution is then heated to the boiling point. The pH, which thereby drops, is adjusted again by adding ammonia free from CO_2.

The uranium is precipitated in the hot solution with 10-13 ml of a 2% alcoholic solution of α-nitroso-β-naphthol. The solution plus precipitate are allowed to stand overnight. On the following day the precipitate is filtered off and carefully washed with cold water until completely colorless wash liquors are obtained. The precipitate is dried, ashed, and calcined gently in a porcelain crucible at 550°. The residue is dissolved in the crucible in a few ml of concentrated hydrochloric acid; the solution is evaporated to a few drops, and the contents of the crucible quantitatively transferred to a 50 ml standard flask. One to two drops of a 10% solution of ammonium thiocyanate is added, and 2% EDTA-Na solution added dropwise until the red color disappears; 10-20 drops of EDTA-Na is then added in excess. Five ml of a 25% solution of urotropine (pH 6, 5-7) is added, followed by 2 ml of a 0.1% solution of bromopyrogallol red in 50% alcohol. The volume of the solution is made up to the mark with twice-distilled water; the whole is carefully mixed, and the optical density is measured on an FÉK-M apparatus with a red filter, using a 3 cm cuvette. During construction of a calibration curve, 2 ml of the 2% solution of EDTA-Na is added to the uranium solutions.

We also used partition chromatography on silica gel [2] for separating uranium from interfering elements. To the test solutions, after removal of interfering elements and prior to the photometric determination, was added 2-5 drops of the 2% EDTA-Na solution. The appropriate amounts of EDTA-Na were also added to the solutions used for constructing the calibration curve.

Photometric Determination of Uranium in Standard Ores by Means of Bromopyrogallol Red

Sample No.	Specified uranium content, %	Separation method	Uranium found photometrically, %	Mean, %
9	0.070	Precipitation with α-nitroso-β-naphthol	0,071; 0,0675; 0,0670; 0,065; 0,067; 0,073; 0,0705; 0,0705; 0,0675	0.069
		Partition chromatography	0,071; 0,070; 0,073; 0,071; 0,070; 0,069; 0,071	0.070
7	0.059	Precipitation with α-nitroso-β-naphthol	0,062; 0,057; 0,065; 0,061; 0,061; 0,059; 0,062; 0,065; 0,055	0.061
		Partition chromatography	0,060; 0,0596; 0,0596; 0,0596; 0,059; 0,060; 0,060; 0,060; 0,0592	0.060
27	0.103	Precipitation with α-nitroso-β-naphthol	0,100; 0,0995; 0,104; 0,100; 0,104; 0,104;	0.102
		Partition chromatography	0,104 ;0,103; 0,104; 0,103; 0,103; 0,103; 0,106; 0,103; 0,102; 0,103	0.103
2	0.22	The same	0,20; 0,21; 0,22; 0,23; 0,21; 0,218; 0,22; 0,218; 0,216	0.215
4	0.072	Precipitation with α-nitroso-β-naphthol	0,073; 0.074; 0,073; 0,075; 0,075; 0,070; 0,070; 0,068	0.072
29	0.0725	The same	0,0775; 0,071; 0,070; 0,070; 0,0737; 0,0703; 0,068	0.072
30	0.22	" "	0,21; 0,218; 0,216; 0,222; 0,205; 0,218; 0,222: 0,21	0.215

The use of the partition chromatographic method of separation gave satisfactory results.

The results obtained during the analysis of standard ores are given in the table.

SUMMARY

A technique has been developed for the photometric determination of uranium in ores by means of bromopyrogallol red.

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AMPEROMETRIC TITRATION OF SEXIVALENT URANIUM WITH DIVALENT CHROMIUM SALTS

Z. A. Gallai and G. E. Kalenchuk

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Most titrimetric methods of determining uranium are based on its oxidation–reduction reactions [1-5]. In amperometric methods of determining uranium, use is made of its precipitation reaction with potassium ferrocyanide [6], or the oxidation reaction of quadrivalent uranium [7]; the experimental accuracy is not high.

Some strong reducing agents (Cr^{2+}, Ti^{3+} [1, 8, 10] reduce sexivalent uranium to the quadrivalent state. We have studied the possibility of titrating sexivalent uranium amperometrically with solutions of divalent chromium salts, which are comparatively readily prepared, and which under certain storage conditions do not change their titer for a long time.

It has been established [11] that divalent chromium ions are oxidized on a rotating platinum microelectrode; the diffusion current at potentials of 0.3-1.1 v* is proportional to the concentration of divalent chromium ions.

The work was carried out on a VP-5 visual type polarograph made by "Geopribortsvetmet." The current was measured with an M-21 mirror galvanometer with a maximum sensitivity of 2.4×10^{-9} a/mm/m.

The rotating platinum microelectrode was prepared from a platinum wire (d = 0.5 mm, l = 5 mm), which was fused into a glass tube with a mercury contact. The electrode was rotated by an electric motor at the rate of 600 rpm. The reference electrode was a saturated calomel electrode connected to the electrolyzer via an agar-agar bridge.

A vibrating microelectrode [12] was used for titrating in small volumes (1-2 ml). Oxygen was removed from the solution by means of nitrogen which had been carefully purified from oxygen [13].

The divalent chromium salt solutions were prepared by a method suggested by Busev [14], using amalgamated zinc as the reducing agent. The $CrCl_2$ and $CrSO_4$ solutions prepared were standardized amperometrically against potassium dichromate [11]. The titer of the solutions did not change over a period of 25-30 days. 0.04195 N $CrCl_2$ and 0.04771 N $CrSO_4$ solutions were used in the work. Uranyl sulfate solution was prepared from the solid salt containing 53.03% U. The solution was acidified with sulfuric acid to a pH of 2.9. The uranium content of the solution was established gravimetrically (ammonia and hydroxyquinoline). The solution contained 12.35 mg U/ml.

The behavior of uranium compounds on a dropping mercury electrode has been studied [1]; the behavior of uranium on a rotating platinum microelectrode, however, has only been studied to a small extent. Rozental' and Veselovskii [15] have pointed out the complexity of the electrochemical oxidation of quadrivalent uranium compounds to the sexivalent state.

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*Relative to the saturated calomel electrode.

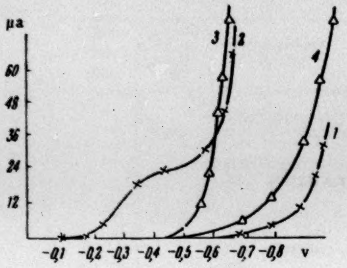

Fig. 1. Reduction of sexivalent uranium on a platinum microelectrode. 1) In a supporting electrolyte of 0.5 N K_2SO_4; 2) U^{VI} in a supporting electrolyte of 0.5 N K_2SO_4; 3) U^{VI} in a supporting electrolyte of an acetate buffer at pH 3.9; 4) in a supporting electrolyte of 0.5 N $(NH_4)_2CO_3$.

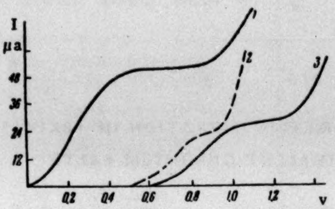

Fig. 2. Oxidation of quadrivalent uranium. 1) U^{IV} in a supporting electrolyte of acetate buffer, pH 3.9; 2) in a supporting electrolyte of 1 N HCl; 3) U^{IV} in a supporting electrolyte of 1 N H_2SO_4.

Reduction of sexivalent uranium on a platinum electrode was carried out in a supporting electrolyte of 0.5 N K_2SO_4; an acetate buffer, pH 3.9; and 0.5 N $(NH_4)_2CO_3$ in a N_2 atmosphere. The volt–ampere curves obtained (Fig. 1) show that the most suitable supporting electrolyte for the reduction of sexivalent uranium is 0.5 N K_2SO_4. Use of the cathodic reduction current of sexivalent uranium during amperometric determinations is strongly limited by the need for strict observance of the composition of the supporting electrolyte.

Quadrivalent uranium compounds were prepared by reduction of uranyl sulfate solution in a cadmium reducer or with $CrCl_2$, the amount of the latter added being such that 60-70% of the uranium was subjected to reduction.

The volt–ampere curves obtained are shown in Fig. 2. Increasing the acidity of the supporting electrolyte shifts the oxidation wave of quadrivalent uranium toward more positive potentials. A proportionality between the value of the diffusion current and the uranium concentration of the solution is only observed when a buffer solution with a pH of 3.9 is used as a supporting electrolyte.

In carrying out amperometric determinations of sexivalent uranium based on reduction of uranium to its quadrivalent state, it is necessary to take into account the possibility of some distortion of the titration curve as a result of the oxidation of the quadrivalent uranium on the electrode when the electrode potential is sufficient for this process to occur.

The reduction of sexivalent uranium by divalent chromium salts has been used earlier for the potentiometric determination of microamounts of uranium, the titration being carried out at 70-80° [9, 10].

Our experiments showed that the reaction between sexivalent uranium and divalent chromium proceeds rapidly enough at room temperature, since the equilibrium values of the diffusion current are established fairly rapidly.

In carrying out amperometric titration a stream of nitrogen was passed through 15 ml of test solution, via a tube with a capillary tip (fine droplets of inert gas expel dissolved oxygen more rapidly) for 20-30 min. Titration was carried out at a potential of ± 0.6 v. As a result of a series of experiments it was established that acid concentration has considerable influence on the experimental accuracy of the determination of sexivalent uranium by means of divalent chromium salts.

When titrations are carried out in a supporting electrolyte of 1-6 N hydrochloric acid, the titration curves have an unusual shape (Fig. 3); initially, an increase in current is observed. Nevertheless, as can be seen from the results given in Table 1, results for the determination of uranium in a supporting electrolyte of 2-5 N HCl are completely satisfactory.

TABLE 1

Titration of Sexivalent Uranium with $CrCl_2$ Solution in a Supporting Electrolyte of HCl

HCl supporting electrolyte, N	U, mg		Error	
	taken	found	mg	%
1	6,16	6,10	—0,06	—1
2	6,16	6,15	—0,01	—0,3
3	6,16	6,15	—0,01	—0,3
4	6,16	6,15	—0,01	—0,3
4	3,36	3,36	0	0

TABLE 2

Titration of Sexivalent Uranium with $CrSO_4$ Solution in a Supporting Electrolyte of H_2SO_4

H_2SO_4 supporting electrolyte, N	U, mg		Error	
	taken	found	mg	%
1	1,30	1,19	—0,11	—8,5
2	3,08	3,07	—0,01	—0,3
2	1,25	1.25	0	0
4	6,04	6,02	—0,02	—0,3
4	5,14	3,17	0,03	0,9
4	3,14	3.13	—0.01	—0,3
6	6,55	6,54	—0,01	—0,2
8	6,17	6,42	0,25	4
4	0,673	0,674	0,001	0.01
4	0,673	0,675	0,002	0,3
4	0,337	0,340	0,003	0,7
4	0,337	0,337	0	0

TABLE 3

Determination of Sexivalent Uranium in the Presence of Pb^{2+}, Zr, and Th in a Supporting Electrolyte of 4 N HCl and 4 N H_2SO_4

Taken, mg				Ratio, element : U	U found, mg	Error	
Pb	Zr	Th	U			mg	%
12	—	—	6,04	1 : 2	6,03	—0,01	-0,1
60	—	—	6,29	1 : 10	6,30	0,01	0,1
50	—	—	1,12	1 : 50	1,13	0,01	0,9
—	300	—	6,06	1 ; 50	6,03	—0,03	—0,5
—	230	—	2,36	1 : 100	2,37	0,01	0,5
—	1200	—	1,23	1 : 1000	1,23	0	0
	—	300	6,16	1 : 50	6,17	0,01	0,1
		500	1,22	1 : 500	1,23	0,01	0,4
		1000	1,22	1 : 1000	1,24	0,02	0.5

TABLE 4

Determination of Sexivalent Uranium and Trivalent Iron in Each Other's Presence in a Supporting Electrolyte of 4 N H_2SO_4

Ratio U : Fe	U, mg		Error, mg	Fe, mg		Error, mg
	taken	found		taken	found	
1 : 1,3*	2,10	2,15	0,05	2,74	2,70	0,04
1 : 1,3	2,10	2,13	0,03	2,69	2,66	—0,03
1 : 5*	2,47	2,47	0	12,04	12,05	0,01
1 : 5	2,47	2,48	0,01	12,04	12,07	0,03
1 : 10	2,47	2,40	—0,07	24,08	24,41	—3
1 : 10	2,47	2,43	—0,04	24,08	24,32	0,24
1 : 50	0,673	0,675	0,02	33,5	33,0	0,5

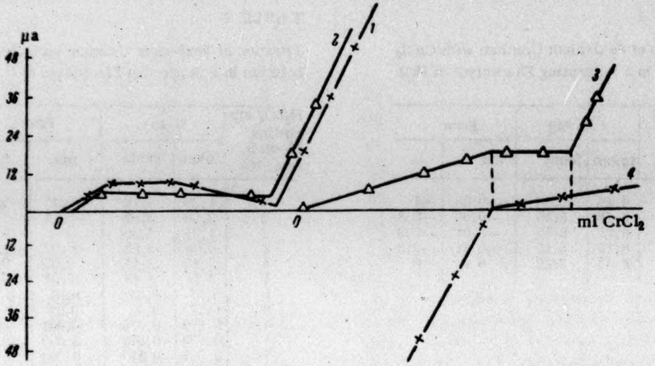

Fig. 3. Titration curves of sexivalent uranium and trivalent iron with divalent chromium salts. 1) U^{VI} in a supporting electrolyte of 4 N HCl, E = 0.5 v; 2) U^{VI} in a supporting electrolyte of 4 N H_2SO_4, E = 0.5 v; 3) U^{VI} and Fe^{III} in each other's presence in a supporting electrolyte of 4 N H_2SO_4; 4) Fe^{III} in a mixture with U^{VI}, E = 0 v.

When the titrations are carried out in a supporting electrolyte of sulfuric acid, the titration curves have the usual shape (Fig. 3), although at the start of the titration there is some increase in the current. During the determination of small amounts of uranium (0.6-0.3 mg), the titration was carried out in a volume of 1.5 ml in a special electrolyzer using a vibrating platinum microelectrode.

The titration results are given in Table 2.

Completely satisfactory results are obtained when the titration is carried out in a supporting electrolyte of 2-6 N H_2SO_4. By decreasing the volume of the solution being titrated during the determination of small amounts of uranium, it is possible to determine tenths of a milligram with satisfactory accuracy.

Results for the determination of uranium in the presence of lead are completely satisfactory right up to ratios of U : Pb = 1 : 50; on increasing the lead concentration further, precipitates of $PbCl_2$ and $PbSO_4$ separate out.

Satisfactory results were obtained for ratios of U : Zr and U : Th = 1 : 1000 (mean error ± 0.3%). Results for the determination of uranium in the presence of these elements are given in Table 3. The titration curves obtained during these determinations have the same shape as those obtained during titration of pure uranyl salts.

The main difficulty in developing a method for the amperometric determination of sexivalent uranium in the presence of trivalent iron was the reduction of the latter to the divalent state prior to the start of the reduction of sexivalent uranium.

During the determination of sexivalent uranium and trivalent iron in each other's presence, iron was first titrated with $CrCl_2$ solution at 0 v, while in another aliquot of the solution the sum of the two elements was titrated at a potential of 0.5 v (Fig. 3). The uranium content was found by difference. Satisfactory results were obtained up to a ratio of U : Fe = 1 : 50.

At ratios of U : Fe up to 1 : 10 it was found possible to determine both elements from one titration curve, since on carrying out titration at a potential of 0.5 v the curve had two sharp breaks, the first corresponding accurately to completion of reduction of trivalent iron, the other corresponding to completion of reduction of quadrivalent uranium (Curve 3, Fig. 3).

The titration results are given in Table 4.

We should like to express our gratitude to I. P. Alimarin for his valuable advice in the course of the work described here.

SUMMARY

A method has been developed for the direct amperometric titration of sexivalent uranium in pure solutions with a solution of a divalent chromium salt, using rotating and vibrating platinum microelectrodes. Lead at ratios up to U : Pb = 1 : 50 and zirconium and thorium at ratios up to 1 : 1000 do not interfere with the determination. The method permits determination of uranium in solutions containing trivalent iron.

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A QUANTITATIVE METHOD FOR THE DETERMINATION OF URANIUM ON THE BASIS OF ITS LUMINESCENCE IN PHOSPHORIC ACID SOLUTIONS

A. V. Davydov, T. S. Dobrolyubskaya, and A. A. Nemodruk

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The method of determining small amounts of uranium on the basis of the luminescence of beads (or alloys) of sodium fluoride [1, 2], which is in widespread use at the moment, is connected with a number of difficulties of a practical nature: the beads or alloys have to be prepared in the loop of a platinum wire or on platinum targets at a high temperature (about 1000°); when such a technique is used the intensity of the luminescence of the bead obtained depends on many factors (temperatures and duration of fusion, the atmosphere during calcining, and the cooling conditions). A quantitative method of determining uranium on the basis of its luminescence in aqueous solution would enable all these drawbacks to be overcome. Melkov and Sverdlov [3] have drawn attention to the fact that many nonluminescent uranium-containing minerals can be converted into a luminescent state by treating their surfaces with various reagents (phosphoric, sulfuric, and other acids); when this is done, uranium compounds are obtained which luminesce predominantly on excitation with short wave ultraviolet light.

In 1947 Levshin and co-workers, and later Novak [4], used the luminescence of uranium in sulfuric acid solutions for analytical purposes. A number of research workers [1, 5] have been occupied with the study of the possibility of testing ores for uranium on the basis of its luminescence in phosphoric acid solutions. Of particular interest in this connection is the work of Sill and Peterson [5].

The aim of the work described here was to develop a quantitative method of determining uranium on the basis of its fluorescence in phosphoric acid solutions, which have a number of advantages over sulfuric acid solutions; the luminescence intensity of sexivalent uranium in phosphoric acid solutions is significantly higher than that in sulfuric acid solutions; phosphoric acid itself does not luminesce on illuminating it with ultraviolet light, while sulfuric acid often luminesces as the result of the presence of organic materials (the luminescence is blue in color); in addition, phosphoric absorbs ultraviolet light to a smaller extent than other acids.

Properties of the luminescence of sexivalent uranium in phosphate solutions. We made a study of the relation between the luminescence intensity of uranyl nitrate solutions (concentration 100 μgU/ml) and the addition of a number of materials (Table 1). Measurements were made on a horizontal Pulfrich photometer, the solution being illuminated from above during excitation with ultraviolet light (253.7 mμ). A BUV-15 bactericide lamp fitted with a UFS-1 filter (for which it is convenient to use a Brumberg UB-1 ultrachemiscope [6]) served as the excitation source. A cuvette in which the distance between the working edges was 5 cm was used.

It is clear from Table 1 that phosphoric acid solutions of uranyl exhibit the highest luminescence intensity; the next in order are solutions containing unisubstituted phosphate, sulfate, and fluoride ions.

We should point out that the luminescence of sexivalent uranium in aqueous solutions is very sensitive to additions of various organic materials (glycerol, ethanol), reducing agents (hydrazine, hydroxylamine), and also to oxidizing agents (hydrogen peroxide), in the presence of which the luminescence intensity drops.

TABLE 1

The Relation between the Luminescence Intensity of Sexivalent Uranium and the Chemical Composition of the Solution

Material added	Amt. of additive, calculated in terms of the anion	Luminescence intensity in relative units
Na_2CO_3	5%	Very weak luminescence
$NaHCO_3$	5%	The same
NaCl	5%	" "
NaI	5%	No luminescence (the solution is yellow)
NaF	Saturated solution	22 (bright luminescence)
$NaHF_2$	" "	20 The same
Na_2SO_4	5%	33 " "
$NaHSO_4 \cdot 2H_2O$	5%	33 " "
$NaH_2PO_4 \cdot 2H_2O$	5%	36 " "
$Na_2HPO_4 \cdot 7H_2O$	5%	6 (weak luminescence)
$Na_3PO_4 \cdot 12H_2O$	5%	2 The same
Sodium acetate	5%	3 " "
Sodium oxalate	5%	No luminescence
Sodium citrate (trisubstituted)	5%	The same
Sodium tartrate (disubstituted	5%	" "
H_3PO_4	5%	100 (bright luminescence)
Sodium arsenite	5%	No luminescence

In Fig. 1 is shown the relation between the logarithm of the luminescence intensity (in relative units) and the concentration of sexivalent uranium in a 5% phosphoric acid solution. It follows from the results obtained that at very low concentrations (down to about 1×10^{-4} g U/ml) there is a linear relation between the luminescence intensity and concentration; on increasing the concentration further, the curve passes through a maximum which is found at about 2.5×10^{-4} g U/ml. Thus, sexivalent uranium can be quantitatively determined on the basis of its luminescence in aqueous phosphoric acid solutions from very low concentrations to about 1×10^{-4} g U/ml.

We tried to explain the increase in the luminescence intensity of sexivalent uranium in phosphoric acid solutions by a change in absorption. On adding phosphoric acid to a nitric solution of uranyl there is observed an increase in absorption (Fig. 2 , where curve 1 corresponds to the absorption of a solution whose uranium concentration is 1 μg/ml, while curve 2 corresponds to the absorption of the same solution, but, containing in addition, another 5% of phosphoric acid). Absorption was measured by means of an SF-4 spectrophotometer in the short wave side of the ultraviolet.

It follows from the results obtained that on addition of phosphoric acid to a nitric acid solution of sexivalent uranium, although there is an increase in absorption, nevertheless the luminescence intensity increases many times more in this case.

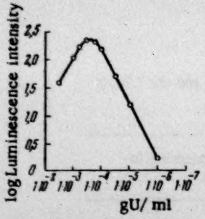

Fig. 1. Relation between luminescence intensity and uranium concentration in a 5% H_3PO_4 solution.

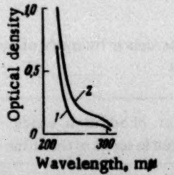

Fig. 2. Absorption curves of U^{VI} in solutions of HNO_3 (1) and a mixture of HNO_3 and H_3PO_4 (2).

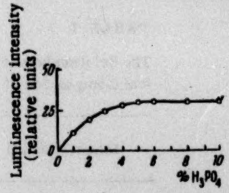

Fig. 3. Relation between the luminescence intensity of uranium in solution and H_3PO_4 concentration.

The luminescence of phosphoric solutions of uranyl is excited by both short wave and long wave ultraviolet light; nevertheless, in the case of dilute solutions (concentration less than 10 μg U/ml) excitation by the short wave ultraviolet (253.7 mμ) gives a considerably higher luminescence intensity. On exciting the luminescence with light from the BUV-15 lamp fitted with a UFS-1 filter it is possible to detect tenths of a gamma of U per ml, while when excitation is effected with a wavelength of 365 mμ the minimum uranium concentration that can be detected is two orders greater (PRK-4 lamp, UFS-3 filter).

One must make the special reservation that in the case of quantitative determination of uranium on the basis of its luminescence in aqueous solutions, the vessels (cuvettes) used should not luminesce when they are illuminated by ultraviolet light. Quartz vessels and vessels made from "pyrex" satisfy these requirements. The luminescence intensity of phosphoric solutions with low uranium contents (from a few tenths of a gamma to 10 μg U/ml) can also be measured by means of the ÉF-3 photoelectric luminescence photometer, which is produced by the Control-Measuring Apparatus factory of the Ministry of the Food Industry (Moscow), in which the primary filter is the UFS-1 filter and the secondary filter is the filter used for Vitamin B_1 determinations. Measurements are made in a quartz tube with a diameter of about 1.5 cm, the position of the latter being strictly fixed.

The luminescence intensity of sexivalent uranium in phosphoric acid solutions increases with decreasing temperature (the studies were made over the range 0 to 90°). In this connection, during quantitative determinations, the standard and test solutions should have the same temperature, e.g., + 20°.

It should also be pointed out that the luminescence intensity of sexivalent uranium in phosphoric acid solutions depends, over a certain range, on the phosphoric acid concentration, as is evident from Fig. 3, in which the phosphoric acid concentration (in percent) is plotted along the abscissa, while the luminescence intensity (in relative units) is plotted on the ordinate; the uranium concentration in solution is 3 μg U/ml.

From Fig. 3 it is clear that on increasing the phosphoric acid concentration to 5% the luminescence intensity of uranium in the solution increases to reach a definite value, which remains constant on increasing the phosphoric acid concentration further.

In the method suggested below, 5% phosphoric acid solutions are recommended.

On adding most of the foreign ions to phosphoric acid solutions of uranyl, the luminescence intensity usually drops. Data on the effect of impurities on the luminescence of uranium are given in the paper by Sill and Peterson [5]. The quenching effect of impurities is more clearly expressed in aqueous solutions than is the case for the determination of uranium on the basis of the luminescence of beads or alloys prepared on a sodium fluoride base. Quantitative determination of uranium on the basis of its luminescence in aqueous phosphate solutions is possible, when the impurities which act as quenching agents are removed (Fe, Cu, Mn, Cr, Ni, Co, etc.).

Separation of uranium from quenching impurities. We used an extraction method for this purpose. The extractant used was tributyl phosphate, which possesses a high selectivity [7, 8], while the diluent was carbon tetrachloride, and calcium nitrate was used as a salting out agent. Quenching impurities were first complexed by addition of sodium ethylenediaminetetraacetate (EDTA-Na). After the uranium had been extracted from the organic phase, it was re-extracted into the aqueous phase and was then determined on the basis of its luminescence in phosphate solutions.

TABLE 2

Limiting Permissible Ratios of Quenching Impurities to Uranium in the Original Solutions

Elements	Composition of the added material	Limiting-permissible ratio of quenching impurity to uranium	
		using EDTA-Na	without addition of EDTA-Na
Fe^{III}	$Fe(NO_3)_3 \cdot 9H_2O$	2500	200
Cr^{VI}	$K_2Cr_2O_7$	100	100
Cr^{III}	$Cr(NO_3)_3 \cdot 9H_2O$	100	100
Ni^{II}	$Ni(NO_3)_2 \cdot 6H_2O$	7500	45
Cu^{II}	$Cu(NO_3)_2 \cdot 6H_2O$	80 000	60
Rare earths	Nitrates	—	250
Th^{IV}	$Th(NO_3)_4 \cdot 4\ H_2O$	4500	90
Ce^{IV}	$Ce(OH)(NO_3)_3 \cdot 3H_2O$	—	200
Zr^{IV}	$Zr(NO_3)_4 \cdot 5H_2O$	8500	450
Mo^{VI}	$(NH_4)_2MoO_4$	200	500
V^V	NH_4VO_3	12 000	400
W^{VI}	$Na_2WO_4 \cdot 2H_2O$	5000	1200
As^V	$Na_3AsO_4 \cdot 12H_2O$	2000	2000

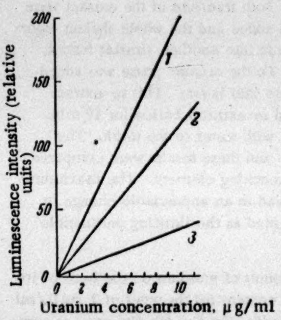

Fig. 4. The relation between the intensity of U^{VI} in solution and the presence of tributyl phosphate and CCl_4. 1) Solutions of U^{VI} in 5% H_3PO_4; 2) re-extract (5% H_3PO_4 after boiling; 3) re-extract (5% H_3PO_4) without boiling.

The reagents used should not luminesce on being illuminated with ultraviolet light, nor should they quench the uranium luminescence.

The use of "pure" grade tributyl phosphate for extracting the uranium leads to lower results when the latter is determined on the basis of its luminescence in the aqueous re-extracts than when purified tributyl phosphate is used; accordingly, the tributyl phosphate was purified. To 100 ml of the commercial tributyl phosphate was added 400 ml of carbon tetrachloride and 750 ml of 1% NaOH solution. The mixture was vigorously shaken, and, after it had separated into two layers, the organic phase was separated; the latter was then washed twice with 750 ml lots of water. To the washed residue was added 5 g of activated charcoal powder ("clarifying" grade), and, after vigorous shaking the residue was passed through folded filter paper. The filtered solution of tributyl phosphate in carbon tetrachloride was washed twice with 750 ml of water, and again filtered through folded filter paper.

Aqueous solutions of EDTA-Na prepared by dissolving varying amounts of the commercial preparation sometimes exhibited an intense blue fluorescence on being illuminated with ultraviolet light, and only EDTA-Na which had been purified by a published method [9], was found to be satisfactory. 0.25-0.5 g of EDTA-Na (depending on the amount of interfering elements) was added to 25 ml of the test solution, the pH of which was adjusted to 2.5-3.0 (by means of HNO_3 or NaOH depending on the reaction of the solution). Under these conditions, elements which, though they are only extracted to a negligible extent by tributyl phosphate from aqueous solution of calcium nitrate, are strong quenchers (iron, copper, etc) are masked by EDTA-Na and remain in the aqueous phase. As a result of this it becomes possible to determine very small amounts of uranium (less than 1 μg U/ml) in solutions containing large amounts of impurities.

Extraction of uranium with an equal volume of a 20% solution of tributyl phosphate in carbon tetrachloride from nitric acid solutions containing 40% $Ca(NO_3)_2 \cdot 4H_2O$ ensures a high percentage extraction of uranium (about 99.9%). Extraction under the same conditions with two successive equal portions of tributyl phosphate in carbon tetrachloride makes it possible to extract uranium quantitatively.

Both pure water and phosphoric acid solutions (from 5 to 10%) proved suitable for re-extraction of the uranium from the organic phase into the aqueous phase.

Since during re-extraction of uranium with 5% phosphoric acid the aqueous phase dissolves the tributyl phosphate and carbon tetrachloride, the luminescence intensity of uranium in these solutions is less than that of phosphoric acid solutions of uranyl of the same concentration, but free from the impurities indicated. Boiling the re-extracts for not less than 2-3 min favors a significant increase in the luminescence intensity of uranium in solution; this is possibly the result of evaporating off the carbon tetrachloride. These regularities are seen in Fig. 4, where curve 1 corresponds to solutions of sexivalent uranium in 5% H_3PO_4, curve 2 corresponds to re-extracts boiled for 5 min, and curve 3 corresponds to re-extracts which had not been boiled beforehand.

Thus, during quantitative determination of uranium on the basis of the luminescence of its aqueous phosphoric acid solutions it is essential that the standard and test solutions be prepared under identical conditions: identical extraction, re-extraction, and subsequent boiling and cooling.

The permissible ratios of quenching impurities to uranium for which it is still possible to determine uranium quantitatively without resorting to the method of "known additions" were determined. These results are given in Table 2; these results were obtained with and without EDTA-Na.

The following experimental procedure was adopted for establishing these ratios. A series of aqueous solutions was prepared containing 40% calcium nitrate, 1 μg U/ml (in the form of uranyl nitrate), and various amounts of the quenching impurities whose influence it was desired to examine. The nitric acid concentration of the solutions was 0.2 M. The method of adding EDTA-Na has been indicated above. To 25 ml of each solution contained in a separating funnel was added 12.5 ml of a 20% solution of tributyl phosphate in carbon tetrachloride; the mixture was vigorously shaken for 2 min and after separation into two layers the organic phase was filtered through dry filter paper. To the aqueous phase remaining in the separating funnel was added another 12.5 ml of the solution of tributyl phosphate in carbon tetrachloride, and the extraction repeated. Both fractions of the extract were transferred to a separating funnel, and 12.5 ml of a 5% phosphoric acid solution added and the whole shaken vigorously for 2 min. After separating into two layers, the lower organic phase was run into another similar funnel, while the aqueous phase remaining was poured into a 60-75 ml quartz beaker. To the organic phase was added another 12.5 ml of 5% phosphoric acid; the whole was shaken and left to separate into layers. This re-extract was combined with the fraction of re-extract obtained earlier and the combined re-extracts boiled for 10 min. After cooling, the solution was transferred to a 25 ml standard flask and diluted with water to the mark. The luminescence intensity of the solutions obtained was measured in relative units and these results were compared with the corresponding results obtained for a uranium solution free from the quenching element. The maximum content of quenching element which in the original test solution still did not lead to an appreciable change in the luminescence intensity of uranium in the re-extract (less than 2%) was accepted as the limiting permissible content.

The method which we have suggested for the determination of small amounts of uranium on the basis of its luminescence in phosphate solutions has been used for determining the uranium content (of the order of 1 μgU/ml and less) of synthetic solutions containing large amounts of quenching impurities (Fe, Cr, Cu, Ni, Co, etc.) as compared to the uranium. The results obtained are characterized by good reproducibility. The experimental accuracy for the determination of about 1 μg U/ml is + 10%. An analysis does not take longer than 25 min.

The authors wish to thank P. N. Palei for his valuable advice and interest.

SUMMARY

A highly sensitive method has been developed for the quantitative determination of uranium, which is based on the luminescence of the latter in phosphoric acid solutions. The method includes the preliminary removal of uranium from quenching impurities by complexing the latter with sodiumethylenediaminetetraacetate, extraction of the uranium with a solution of tributyl phosphate in carbon tetrachloride (salting out agent calcium nitrate), with subsequent re-extraction of the uranium into the aqueous phase by a phosphoric acid solution and determination of the uranium on the basis of its luminescence intensity in the re-extract obtained.

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THE USE OF SELENOUREA IN ANALYSIS

COMMUNICATION II. PHOTOMETRIC DETERMINATION OF RUTHENIUM AND OSMIUM BY MEANS OF SELENOUREA WITHOUT THEIR PRELIMINARY SEPARATION. THE COMPOSITION AND STABILITY OF THE SELENOUREA COMPLEX OF RUTHENIUM*

A. T. Pilipenko and I. P. Sereda

T. G. Shevchenko Kiev State University

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Several photometric methods are known for the determination of ruthenium. The simplest of them, but the least selective, are methods based on measurement of the color of K_2RuCl_5 [1] and ruthenate in an alkaline medium [2]. During the determination of ruthenium by means of p-nitrosodimethylaniline [3] and 1,10-phenanthroline [4], ruthenium must be separated beforehand by distillation as RuO_4. Thiourea [5-9], dithiooxamide [10, 11], thiocyanate [12], and many derivatives of thiourea and thiosemicarbazide [13-15] have also been used for the photometric determination of ruthenium. In strongly hydrochloric acid media, on heating, these reagents form blue colored compounds with ruthenium [17].

Osmium also reacts with sulfur-containing reagents. The compounds of osmium with these reagents are characterized by a narrower absorption band, which is shifted toward the short wave part of the spectrum, while the analogous compounds of ruthenium possess a wider absorption band which is shifted toward the long wave part of the spectrum. Thus, ruthenium can be determined in the presence of osmium, but in order to determine osmium it is always necessary to separate ruthenium.

In the first communication [16] it was shown that selenourea, like thoiurea, reacts with many heavy metals to form colored compounds. Selenourea also forms soluble, colored complexes with ruthenium and osmium. The present article is devoted to results on the determination of the composition and stability of the selenourea complex of ruthenium, and a description is given of a selenourea method for the determination of ruthenium and osmium without their preliminary separation.

The effect of acidity on the formation of the selenourea complexes of ruthenium and osmium. In order to clarify the effect of acidity on the formation of the selenourea complexes of ruthenium and osmium, experiments were carried out as follows. To a constant volume of a solution of the metal salt was added a constant amount of a selenourea solution and various amounts of concentrated hydrochloric acid. The solutions were then diluted with 1 M hydrochloric acid to 10 ml, they were thoroughly mixed, and the optical density of the selenourea complex of ruthenium measured at 760 mμ, and that of osmium at 600 mμ, i.e., in the region of their maximum absorption (Fig. 1). From Fig. 2 it is clear that the optimum acidity for the formation of the selenourea complex of osmium is 1 N HCl, while that for ruthenium is 7 N HCl. A solution with an acidity as high as this is not convenient in practice; accordingly, ruthenium was determined at 6 N HCl.

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*For Communication I, see Zhur. Anal. Khim. 13, 3 (1958).

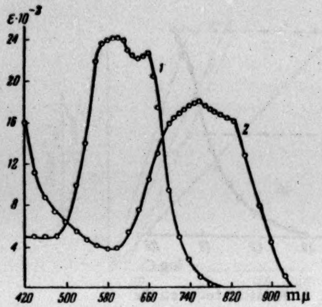

Fig. 1. The absorption curves of the selenourea complexes of osmium (curve 1) and ruthenium (curve 2). The selenourea concentration of the solutions is equal in both cases to 0.2 M.

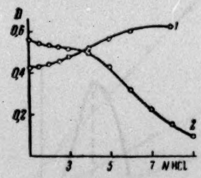

Fig. 2. The relation between the formation of the selenourea complexes of ruthenium (curve 1) and osmium (curve 2), and hydrochloric acid concentration. The concentrations of the reactants in the final volume were: osmium, 2.5×10^{-4} M; selenourea, 1×10^{-1} M; ruthenium, 8×10^{-4}M; selenourea 1.5×10^{-1} M.

Thiourea speeds up the formation of the colored selenourea complex of osmium somewhat and stabilizes the selenourea complex of ruthenium. Because of this, for the determination of osmium and ruthenium urea was added to the test solution first, and selenourea then added.

The composition of the selenourea complex of ruthenium was determined by the isomolar series method [18]. It is clear from Fig. 1 that the composition of the compound is best studied in the spectral region 720-800 mμ; all the other components of the system do not absorb light in this spectral region.

Solutions (0.01 M) of ruthenium and selenourea were prepared in order to determine the composition of the complex. The hydrochloric acid concentration in both solutions was 1 N. These solutions were then mixed in various proportions and concentrated hydrochloric acid added so that its concentration in the final volume was 6 N; the total volume was kept constant. The optical density of the solutions was measured at 760 mμ on an SF-4 spectrophotometer. From Fig. 3 it is clear that the composition of the selenourea complex of ruthenium corresponds to a ratio of the reactants* of $[Ru^{4+}] : [Sem] = 1 : 3$.

The sharp break on the left hand side of the curve shows that the compound of ruthenium with a ratio of ruthenium and selenourea less than 1 : 2 does not exhibit light absorption in this region.

The stability of the selenourea complex of ruthenium. Formation of the selenourea complex of ruthenium can be represented by the scheme:

$$\underset{\text{colorless}}{\mathrm{Ru\ Sem}_x^{4+}} + n\,\mathrm{Sem} \rightleftharpoons \underset{\text{colored}}{\mathrm{Ru\ Sem}_{x+n}^{4+}} \tag{1}$$

The instability constant of the complex will be of the form:

$$K = \frac{[\mathrm{Ru\ Sem}_x^{4+}]\,[\mathrm{Sem}]^n}{[\mathrm{Ru\ Sem}_{x+n}^{4+}]} \tag{2}$$

The extent to which the ruthenium is bound in the colored compound depends on the selenourea concentration.

The numerical value of the instability constant of the selenourea complex of ruthenium was calculated in the same way as that of the selenourea complexes of bismuth [16]. For this purpose** solutions were prepared which

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*$\mathrm{Se = C}\begin{smallmatrix}\diagup \mathrm{NH_2} \\ \diagdown \mathrm{NH_2}\end{smallmatrix}$ will be denoted hereinafter by Sem.

**A solution of $RuOHCl_3$ prepared as described in [19] was used. It might be assumed that quadrivalent ruthenium is reduced by selenourea to trivalent ruthenium, which also forms a selenourea complex. Experiments showed, however,

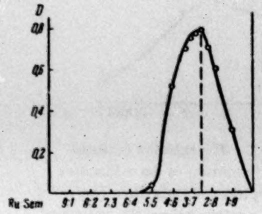

Fig. 3. Composition–optical density curve of the selenourea complex of ruthenium.

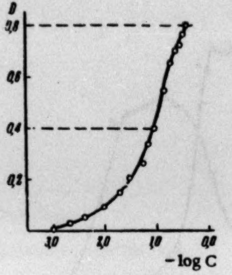

Fig. 4. Relation between the optical density of solutions of the selenourea complex of ruthenium and selenourea concentration.

TABLE 1

Formation of the Colored Selenourea Complex of Ruthenium as a Function of Excess Selenourea

$[\mathrm{Sem}]_{\mathrm{total}}$	$[\mathrm{Sem}]_{\mathrm{excess}}$	$-\log[\mathrm{Sem}]_{\mathrm{excess}}$	D	$[\mathrm{Ru\ Sem}_{x+n}^{4+}]$	$-\log\dfrac{[\mathrm{Ru\ Sem}_{x+n}^{4+}]}{[\mathrm{Ru}_{\mathrm{total}}^{4+}]-[\mathrm{RuSem}_{x+n}^{4+}]}$
0,001	$9,9\cdot10^{-4}$	3,0	0,005	$0,03\cdot10^{-4}$	2,22
0,002	$1,98\cdot10^{-3}$	2,7	0,036	$0,22\cdot10^{-4}$	1,34
0,004	$3,89\cdot10^{-3}$	2,41	0,058	$0,36\cdot10^{-4}$	1,11
0,006	$5,87\cdot10^{-3}$	2,23	0,067	$0,42\cdot10^{-4}$	1,04
0,008	$7,86\cdot10^{-3}$	2,10	0,077	$0,48\cdot10^{-4}$	0,97
0,01	$9,84\cdot10^{-3}$	2,01	0,088	$0,55\cdot10^{-4}$	0,91
0,02	$1,97\cdot10^{-2}$	1,71	0,150	$0,94\cdot10^{-4}$	0,64
0,04	$3,96\cdot10^{-2}$	1,54	0,218	$1,36\cdot10^{-4}$	0,43
0,06	$5,94\cdot10^{-2}$	1,23	0,257	$1,60\cdot10^{-4}$	0,33
0,08	$7,94\cdot10^{-2}$	1,10	0,335	$2,10\cdot10^{-4}$	0,14
0,10	$9,92\cdot10^{-2}$	1,0	0,415	$2,60\cdot10^{-4}$	−0,03
0,15	$1,49\cdot10^{-1}$	0,83	0,550	$3,14\cdot10^{-4}$	−0,23
0,20	$1,99\cdot10^{-1}$	0,70	0,660	$4,12\cdot10^{-4}$	−0,67
0,25	$2,49\cdot10^{-1}$	0,60	0,700	$4,37\cdot10^{-4}$	−0,84
0,30	$2,99\cdot10\ ^{1}$	0,52	0,730	$4,56\cdot10^{-4}$	−1,02
0,35	$3,49\cdot10\ ^{1}$	0,46	0,770	$4,82\cdot10^{-4}$	−1,41
0,40	$3,98\cdot10^{-1}$	0,40	0,800	$5,0\cdot10^{-4}$	—
0,45	$4,43\cdot10^{-1}$	0,35	0,800	$5,0\cdot10^{-4}$	—

contained a constant amount of ruthenium equal to 5×10^{-4} M while the selenourea concentration was increased all the time; the optical density was measured at 760 mμ 30 min after pouring the solutions together. The acidity of the solutions was 6 N with respect to HCl in all cases. Water was used as the reference solution. The results obtained are given in Table 1 and in Fig. 4.

The concentration of the colored ruthenium complex was determined in the same way as the concentration of the colored bismuth complexes [16].

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that $RuOHCl_3$ electrolytically reduced to $RuCl_3$ [19] only partially reacts with selenourea to form a colored reaction product. This apparently results from the presence of insignificant amounts of quadrivalent ruthenium in the chloride of trivalent ruthenium.

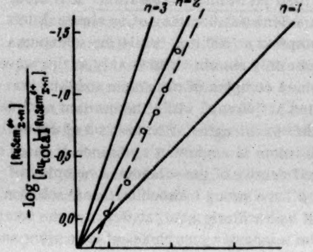
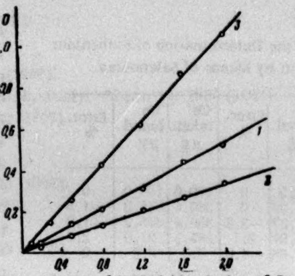


Fig. 5. The effect of excess selenourea on the formation of the selenourea complex of ruthenium.



Amt. in ml of 0.0001 M solution of Os
Amt. in ml of 0.0035 M solution of Ru

Fig. 6. Calibration curves: for ruthenium at 760 mμ (curve 1) and at 600 mμ (curve 2); for osmium at 600 mμ (curve 3).

Reasoning in the same way, we get the following equation:

$$d\log\frac{[\mathrm{Ru\,Sem}^{4+}_{x+n}]}{[\mathrm{Ru}^{4+}_{\mathrm{total}}]-[\mathrm{Ru\,Sem}^{4+}_{x+n}]} : d\log[\mathrm{Sem}] \qquad (3)$$

Equation (3) corresponds to that for a straight line. When the values of the ratio of the negative logarithms of the concentration of the complex to the concentration of free ruthenium which has not been converted into the colored compound are plotted on the same scale on the graph, the slope of the straight line corresponds to n.

As can be seen from Fig. 5, formation of the colored selenourea complex of ruthenium depends on the square of the selenourea concentration.

Taking into account all that has been said above, the equation for the formation of the colored selenourea complex of ruthenium can be depicted as follows:

$$\underset{\text{colorless}}{\mathrm{RuSem}^{4+}} + 2\,\mathrm{Sem} \rightleftarrows \underset{\text{colored}}{\mathrm{RuSem}_3^{4+}}, \qquad (4)$$

from which

$$K_{\mathrm{RuSem}_3^{4+}} = \frac{[\mathrm{RuSem}^{4+}]\,[\mathrm{Sem}]^2}{[\mathrm{RuSem}_3^{4+}]} \qquad (5)$$

When half of the ruthenium has been bound as the colored compound, the numerical value of the instability constant is equal to the square of the excess selenourea concentration. The excess selenourea concentration is found from the curve in Fig. 4. The optical density corresponding to the complexing of half the ruthenium into a colored complex will be

$$\frac{0.800}{2} = 0.400.$$

Such a value for the optical density corresponds to a concentration of excess selenourea of 10^{-1} M, while an approximate numerical value of the instability constant of the complex will be equal to:

$$K_{\mathrm{RuSem}_3^{4+}} = \frac{[\mathrm{RuSem}^{4+}]\,[\mathrm{Sem}]^2}{[\mathrm{RuSem}_3^{4+}]} = (10^{-1})^2 = 10^{-2}$$

The value of the instability constant of the selenourea complex of ruthenium shows that the selenourea complex of ruthenium dissociates to a considerably greater extent than the thiourea complex of ruthenium [20]. All the same, selenourea has an advantage over thiourea in that it permits simultaneous determination of ruthenium and osmium without their separation.

TABLE 2

Results for the Determination of Ruthenium and Osmium by Means of Selenourea

Ru taken, μg	Ru found, μg	Error, %	Os taken, μg	Os found, μg	Error, %
353:5	353,5	0	190,0	190,0	0
35,35	35,35	0	380,4	374,3	—1,5
530,02	512,57	—3,3	380,4	376,2	—1,0
777,7	798,91	2,7	285,3	291,0	2,0
176,75	169,68	—4,0	0,0	0,0	0

Determination of ruthenium and osmium by means of selenourea without their preliminary separation. It is clear from Fig. 1 that the selenourea complex of osmium exhibits maximum light absorption at 600 mμ while the selenourea complex of ruthenium only absorbs light weakly at this wavelength. The selenourea complex of ruthenium exhibits maximum light absorption at 760 mμ while the osmium complex does not absorb at this wavelength. The method of determining ruthenium and osmium in eachother's presence is based on measuring the optical density of the selenourea complex of ruthenium at 760 mμ in a strong hydrochloric acid solution. Subsequently, in 1 N hydrochloric acid, at 600 mμ, the total optical density of the selenourea complexes of ruthenium and osmium is measured; knowing the ruthenium content, the optical density corresponding to ruthenium at 600 mμ is subtracted from the total optical density and the osmium content found.

Urea was added to stabilize the selenourea complex of ruthenium and to accelerate the formation of the selenourea complex of osmium.

Experimental procedure. To 2.5 ml of the test solution which is 1 N with respect to hydrochloric acid is added 4.5 ml of concentrated hydrochloric acid (the hydrochloric acid concentration in the final volume should be about 6 N) followed by 1 ml of 5 M urea solution and 2.0 ml of 0.5 M selenourea solution. Half an hour after preparing the solutions, the optical density is measured at 760 mμ. The colored solutions are stable for 45 min; after this period the solutions become turbid and the optical density increases. The ruthenium content is found by means of a calibration curve constructed beforehand.

In order to determine osmium, to 2.5 ml of the test solution which is 1 N with respect to hydrochloric acid is added 0.5 ml of 5 M urea solution and 2 ml of 0.5 M selenourea in 1 N HCl. The color intensity is measured at 600 mμ half an hour after preparing the solution. Knowing the ruthenium content, the optical density found by means of the calibration curve for the given amount of ruthenium at 600 mμ is subtracted and the osmium content found by the calibration curve.

The calibration curves are shown in Fig. 6.

In Table 2 are given some results obtained during the determination of ruthenium and osmium in synthetic mixtures by this method.

It is clear from this table that the experimental errors for the determination of ruthenium and osmium are quite permissible.

Determination of ruthenium and osmium takes 45-60 min. The method permits determination of 2 to 60 μg Ru/ml and from 2 to 60 μg Os/ml.

The other platinum metals, with the exception of very large amounts of palladium, do not interfere.

SUMMARY

The composition and stability of the selenourea complex of ruthenium have been studied. It has been established that selenourea forms with ruthenium a colored compound which exhibits maximum light absorption at 760 mμ; the ratio of the components in this compound $[Ri^{4+}] : [Sem] = 1 : 3$.

The stability of the selenourea complex of ruthenium is characterized by the following approximate numerical value of its instability constant:

$$K_{RuSem_3^{4+}} = \frac{[RuSem^{4+}]\,[Sem]^2}{[RuSem_3^{4+}]} = 10^{-2}$$

A method has been developed for the determination of ruthenium and osmium without their preliminary separation. Using this method it is possible to determine from 2 to 60 μg Ru/ml and the same amounts of osmium in the presence of the platinum metals, apart from very large amounts of palladium.

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*Original Russian pagination. See C. B. translation.

PHOTOMETRIC DETERMINATION OF NITROGEN IN TITANIUM CARBIDE AND BORIDE AND IN OTHER REFRACTORY MATERIALS

A. Kh. Klibus and T. N. Nazarchuk

Institute of Metallo-Ceramics and Special Alloys, Kiev

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Most of the methods in current use for determination of nitrogen include its lengthy separation from the other components of the test sample by distilling it off as ammonia from an alkaline solution. It is considerably more convenient to use phenol and its homologs and hypochlorite or hypobromite. This reaction has been used mainly for the determination of ammonia in water [1-3]. Lapin and Gein [4] replaced phenol by thymol and hypochlorite by hypobromite. The colored compound formed in this case is extracted with organic solvents; the color of the aqueous layer and possible separation of precipitates in the aqueous layer do not interfere, according to the observations of these authors. The overwhelming majority of cations and anions do not interfere with nitrogen determination [5]; thus the method has a high selectivity. Veinberg [6, 7] has used the thymol-hypobromite reaction for ammonia for the determination of nitrogen in steels. Nevertheless, he has not indicated what the acidity of the solution should be in order to carry out the reaction for ammonia, so that it is not possible to reproduce his technique.

The aim of the work described here was to study the conditions for carrying out the thymol-hypobromite reaction for ammonia and its application to the determination of nitrogen in titanium carbide and other refractory materials.

EXPERIMENTAL METHOD

1. Extraction of the dye formed as a result of the thymol-hypobromite reaction for ammonia with various organic solvents. Diethyl and diisopropyl ether are normally recommended for the extraction [5, 7].

We examined the solubility of the dye formed in various organic solvents. The following results were obtained:

a) Carbon tetrachloride, chloroform, dichloroethane, benzene, toluene, and o-xylene extract the dye from the aqueous layer to form pale orange colored solutions. Separation into layers proceeds readily.

b) Diethyl ether, isoamyl acetate, and diisopropyl ether extract the dye to form bright rose colored solutions. Separation into layers occurs readily, except in the case of diisopropyl ether.

c) n-Butanol and isoamyl alcohol extract the dye from aqueous solutions to give emerald green colored solutions. Separation proceeds readily. On adding the water-soluble alcohols ethanol, methanol, and glycerol to the opaque alkaline aqueous solution of the dye, which is blue in color, the solution acquires an emerald green color and becomes transparent.

These experiments showed, therefore, that brightly colored extracts are obtained on using ethers and alcohols. Of the ethers and esters tested, we settled on isoamyl acetate, which has a lower volatility and on using which the layers separate readily while of the alcohols we chose n-butanol, since the color of the layer obtained with n-butanol, for the same nitrogen content, is brighter than that obtained with isoamyl alcohol.

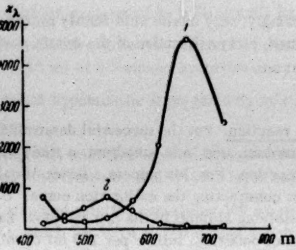

Fig. 1. Absorption curves of extracts of thymolindophenol in n-butanol (1) and in isoamyl acetate (2).

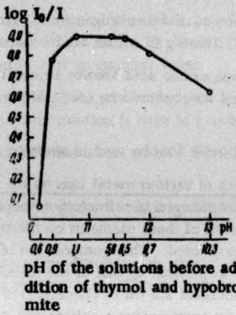

Fig. 2. The relation between the optical density of n-butanol extracts of thymolindophenol and the pH of the solution, before and after addition of thymol and hypobromite.

The absorption curves of solutions of the dye in n-butanol and in isoamyl acetate* are shown in Fig. 1. The arbitrary molar extinction coefficient of the dye in n-butanol is six times that in isoamyl acetate. Accordingly, by using n-butanol for extracting the dye, it is possible to increase the selectivity of the determination. A red filter ($\lambda_{\text{effective}}$ = mμ) should be used for measuring the optical density of the extracts.

2. Establishment of the acidity conditions. The optimum pH value for formation of the dye was established as follows. Equal amounts of ammonium sulfate solution were introduced into a series of flasks and alkali or acid added dropwise for establishing varying pH values, which were measured with an LP-3 pH-meter. An exactly similar series of solutions was then prepared, and thymol and hypobromite added to them. After 30 min the pH of each of them was measured. The dye formed was extracted with 20 ml of n-butanol, and the optical density of the extract measured in a cuvette with a layer thickness of 1 cm.

The results obtained are shown in Fig. 2.

Formation of the colored compound proceeds at pH 11-11.5. For the reaction to proceed successfully, the pH of the test solution should be adjusted to 1.5-8.5 prior to addition of the solutions of the reagents. In practice, good results are obtained on neutralizing the test solution to a phenolphthalein end point.

3. The use of masking agents. The hydroxides of a number of metals adsorb the dye formed and complicate its extraction with organic solvents. In addition, precipitation of such hydroxides as ferric hydroxide interferes with the neutralization of the solutions by alkali to the phenolphthalein end point. Accordingly, during the determination of small amounts of nitrogen it is necessary to prevent precipitation of the hydroxides by addition of appropriate materials.

Of the masking agents tested for iron (Seignette salt, oxalic acid, sodium ethylenediaminetetraacetate, phosphoric acid, and potassium fluoride), potassium fluoride proved to be the most suitable; it does not interfere with the thymol-hypobromite reaction for ammonia.

Potassium fluoride and hydrogen peroxide were tested as agents for prevention of titanium hydroxide precipitation. It was established that hydrogen peroxide in the amounts necessary for completely complexing titanium (0.15 M and upwards) interferes with formation of the dye. Good results were obtained on using potassium fluoride. When the latter is used, during extraction, as a result of a decrease in solubility following upon addition of n-butanol, a white crystalline precipitate of K_2TiF_6 separates out, but this does not interfere with the extraction.

For the determination of nitrogen in samples based on iron and titanium, it is necessary to add 2 ml of a 20% solution of potassium fluoride for completely complexing 0.01 g of iron, while for complexing 0.01 g Ti, 0.5 ml of the potassium fluoride solution should be added.

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*The optical density of the solutions was measured on an FM-Pulfrich type photometer.

During determination of nitrogen in metallic chromium and its compounds, good results are obtained on using oxalic acid. Three g of oxalic acid is necessary for completely complexing 0.01 g Cr.

During storage, oxalic acid absorbs ammonia from the air; accordingly, only oxalic acid freshly recrystallized from twice distilled water should be used. When a high blank is obtained, recrystallization of the oxalic acid should be repeated.

Potassium fluoride can be used in addition to oxalic acid.

4. The effect of various metal ions on the thymol-hypobromite reaction. For the successful determination of small amounts of nitrogen in refractory compounds of titanium, chromium, iron, and vanadium, a study was made of the influence of these elements on the thymol-hypobromite reaction. For this purpose a series of calibration curves was constructed. The composition of the solutions used for constructing the calibration curves corresponded as closely as possible to that of the solutions obtained after dissolving aliquots of the test samples. Each of the solutions contained 2.5 ml of concentrated sulfuric acid and 2 g of potassium sulfate per 100 ml of solution. The solution used for constructing a calibration curve for nitrogen in the presence of titanium contained 0.08 g of titanium in the form of K_2TiF_6, while that used for determination of nitrogen in the presence of chromium contained 0.1 g chromium in the form of $CrCl_3$, that used for nitrogen in the presence of iron contained 0.1 g iron taken in the form of metallic iron, and that used for nitrogen in the presence of vanadium contained 0.1 g of vanadium in the form of V_2O_5.

Ten ml lots of one of these solutions were poured into a series of flasks, to which were then added various amounts (0.1, 0.2. . . 0.8 ml) of a standard ammonium sulfate solution containing 100 μg of nitrogen per ml. In addition, a separate calibration curve was constructed for solutions containing only sulfuric acid, potassium sulfate, and the standard ammonium sulfate solution.

To the solutions obtained was added a 20% potassium fluoride solution and the procedure described for the determination of nitrogen in titanium carbide then followed (see below).

Experiments showed that calibration curves constructed in the presence of titanium, iron, chromium, and vanadium hardly differ at all from the curves obtained under the same conditions with the pure ammonium salt. Accordingly, it is possible to determine small amounts of nitrogen in samples containing titanium, iron, chromium, and vanadium by constructing one general calibration curve, using a pure ammonium salt for its construction.

Below is given a technique for the determination of nitrogen in titanium carbide and boride which has been developed on the basis of the results obtained. Determination of nitrogen in refractory compounds based on chromium, iron, and vanadium only differs in the method used for decomposing aliquots of test sample and in the masking agent used for prevention of hydroxide precipitation.

In refractory chromium compounds nitrogen may be present as the nitrides Cr_2N and CrN. The nitride Cr_2N is readily decomposed on boiling an aliquot of sample with sulfuric acid 1 : 4, while the nitride CrN does not dissolve even on prolonged boiling of an aliquot with a mixture of concentrated sulfuric acid and potassium sulfate [8]. Fusion in this case would lead to volatilization of nitrogen. Since the test samples contain a very small amount of nitrogen compared with their chromium content, it is most likely that the nitrogen in a sample is in the form of Cr_2N. Accordingly, during the determination of nitrogen in refractory chromium compounds, the time for which an aliquot is boiled with sulfuric acid 1 : 4 is limited to two hours. Oxalic acid is added to keep chromium in solution.

During determination of nitrogen in metallic iron and its compounds, the sample is dissolved in sulfuric acid 1 : 4, with subsequent complexing of iron to a fluoride complex.

Since vanadium nitride is decomposed with a mixture of concentrated and potassium sulfate, an aliquot of test samples based on vanadium is boiled with the given mixture for six hours, the solution obtained being analyzed even if complete decomposition is not achieved. Potassium fluoride is used for keeping vanadium in solution.

Determination of nitrogen in titanium carbide. During determination of small amounts of nitrogen in titanium carbide, it is essential, as far as possible, to use chemically pure grade reagents, while all solutions should be prepared in twice distilled water (after adding $KMnO_4$ to a definite rose color and 5 ml of sulfuric acid 1 : 4; the middle fraction of the second distillation is taken).

When chemically pure sodium hydroxide is not available, a 40% solution of it which is free from nitrogen can be prepared as follows: to a 20% solution of sodium hydroxide is added 3-5 lumps of chemically pure zinc, and the solution evaporated by boiling until its volume has decreased to half its original value.

Thymol (2% solution) is prepared by dissolving 2 g of the chemically pure product, ground beforehand in a mortar, in 10 ml of 8% sodium hydroxide and adding 90 ml of water. The solution is kept in a dark vessel.

Sodium hypobromite is prepared by mixing 100 ml of saturated bromine water with 35 ml of 8% sodium hydroxide.

After use, n-butanol can be recovered by distillation, after adding anhydrous calcium chloride to it until saturation and removing the aqueous layer formed.

A standard solution containing 100 μg nitrogen per ml is prepared by dissolving in water 0.4717 g of $(NH_4)_2SO_4$ which has been recrystallized and dried over concentrated sulfuric acid. The solution is transferred to a 1 liter standard flask, and the volume made up to the mark with water.

Analytical procedure. A 0.1 g of titanium carbide is dissolved in 2.5 ml of concentrated sulfuric acid to which 2 g of potassium sulfate has been added; the aliquot is dissolved in a 50 ml flask which is covered with a funnel containing a plug of glass wool, in order to prevent sputtering. After dissolution is complete, the solution is transferred to a 100 ml standard flask, then diluted to the mark with water and thoroughly mixed. Ten ml of the solution obtained is transferred to a 50 ml flask, 0.5 ml of 20% potassium fluoride is added, followed by one drop of phenolphthalein solution; the solution is then neutralized with 8% sodium hydroxide solution until a stable rose color is obtained. Five ml of thymol solution is added and the solution mixed; 5 ml of hypobromite solution is added dropwise with constant stirring, and finally another 5 ml of thymol solution added. After 30 min, the solution is transferred to a 100 ml separating funnel and the blue dye formed extracted with n-butanol 2-3 times using 5-7 ml lots.

The extracts are filtered through a cotton wool plug into a 25 ml standard flask and the volume made up to the mark with n-butanol. The solution is shaken up and the color intensity of the solution obtained measured in a cuvette with a layer thickness of 1 cm.

The nitrogen content is found from a calibration curve constructed by means of the standard ammonium sulfate solution. A blank test is carried out at the same time as the analysis of test samples, taking all the reagents used through all the stages of the analysis.

During measurement of the optical density of the extracts obtained from aliquots of the samples, the extract obtained during the blank run is placed in the other cuvette as reference solution.

SUMMARY

A study has been made of the extraction with various organic solvents of the dye formed during the thymol-hypobromite reaction for nitrogen. n-Butanol gives the most intense color.

The optimum pH for formation of indothymol is 11. Prior to addition of thymol and hypobromite, the acid solutions of the test sample should be neutralized with sodium hydroxide to the phenolphthalein end point.

For prevention of hydroxide precipitation, oxalic acid is used in the case of chromium and potassium fluoride is used for iron, titanium, and vanadium. Iron, vanadium, and titanium as their fluoride complexes and chromium as its oxalate complex do not affect the thymol-hypobromite reaction. A method has been developed for the determination of small amounts of nitrogen (from 0.01 to 1%) in titanium carbide.

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ELEMENTAL ORGANIC ANALYSIS BY THE "WET COMBUSTION" METHOD*

COMMUNICATION II. RAPID DETERMINATION OF SILICON IN SILICOORGANIC COMPOUNDS

A. P. Terent'ev, S. V. Syavtsillo, and B. M. Luskina

M. V. Lomonosov Moscow State University

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Wet oxidation methods have been used for a long time for the analysis of silicoorganic materials [2]. Kreshkov and Nessonova [3] have pointed out that the conditions and the possibilities of oxidation by the wet method are specific for each organic material. Accordingly, in order to oxidize the esters of orthophosphoric acid they used potassium iodate in a sulfuric acid medium, while for diethyl- and diphenyldichlorosilane they used a more complicated mixture consisting of chromic anhydride and potassium iodate in a concentrated sulfuric and phosphoric acid medium. The silica formed in all cases was determined gravimetrically or colorimetrically in the form of blue silicomolybdate.

At present, determination of silicon in polysiloxanes is carried out by heating them with a mixture of 25% oleum and concentrated nitric acid containing 20% nitrogen oxides. The operation is carried out very carefully in order to avoid foaming and sputtering of test samples. After removing the nitrogen oxides and sulfuric acid, the quartz vessel in which oxidation is carried out is calcined to constant weight at 800° and the silicon content assessed from the weight of SiO_2. This method is characterized by the simplicity with which it can be carried out and by its high accuracy (0.2%); it takes a long time, however (7-8 hr) [4].

Šír and Komers [5] also decomposed silicoorganic materials with a mixture of oleum and fuming nitric acid, but a titrimetric finish was used for determining the silicon; this should speed up the analysis. Nevertheless, the necessity of fusing the silica formed with potassium and sodium carbonates in order to convert the SiO_2 to a soluble state increases the overall duration of an analysis.

Earlier [1] we developed a method for the determination of carbon and silicon in silicoorganic compounds on one aliquot. In contrast to the technique of Kreshkov and Nessonova [3], we carried out oxidation with concentrated sulfuric acid and a concentrated aqueous solution of chromium trioxide in an oxygen stream at 150°. Under these conditions even such stable materials as polysiloxanes were completely oxidized. Complete mineralization in the latter instance was achieved considerably more rapidly (30 min) than is possible by the existing method [4]. During the oxidation, resinification and sulfonation products were not formed, such compounds being often more stable to oxidation than the compounds originally taken. At the same time the mineralized silica was determined gravimetrically; this took 3-3.5 hr.

Thus, the short method of decomposing silicoorganic materials [1] ended in a long gravimetric determination of silica, while a rapid titrimetric finish was used in conjunction with prolonged decomposition [5].

Kalman and Vago [6] have successfully used a titrimetric determination of silicon in tetraethoxysilane. The method suggested by the authors is based on the hydrolysis of tetraethoxysilane in an alcoholic solution of hydrofluoric

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*For Communication I, see [1].

TABLE 1

Determination of Silicon in Silicoorganic Compounds after Oxidation with a Chromic and Sulfuric Acid Mixture

Test compound	Sample wt., mg	0.1 N HCl used, ml	Si, %		Difference
			found	calc.	
1,8-Triethylethyloctasiloxane $C_{36}H_{90}O_7Si_8$	27,20 25,40	10,20 9,41	26,31 25,99	26,13	+0,18 —0,14
1,3,5,7-Diethylcyclotetrasiloxane $C_{16}H_{40}O_4Si_4$	28,45 26,70	11,20 10,41	27,62 27,35	27,48	+0,14 —0,13
Dimethyldidecyloxysilane $C_{22}H_{48}O_2Si$	90,60 90,40	9,61 10,00	7,44 7,76	7,54	—0,10 +0,22
Trimethyldecyloxysilane $C_{13}H_{30}OSi$	101,20 98,80	16,96 16,81	11,76 11,94	12,19	—0,43 —0,25
Phenyldibutoxychlorosilane $C_{14}H_{23}O_2SiCl$	46,50 48,00	6,46 6,81	9,75 9,95	9,79	—0,04 +0,16
Phenylmethylbutoxychlorosilane $C_{11}H_{17}OSiCl$	43,10 36,90	7,64 6,26	12,44 11,90	12,28	+0,16 —0,38

TABLE 2

Determination of Silicon in Technical Ethylpolysiloxanes

Sample designation	Sample wt., mg	0.1 N HCL used, ml	Si determined, %		Deviation between the methods, %
			by the method proposed	by the current method	
Type 5, batch 3	13,25 22,70	5,13 8,89	27,2 27,5	26,9	0,4
Type 4, batch 2	18,60 32,00	7,64 13,37	28,8 29,3	28,4	0,6
Liquid 1, batch 7	21,10 21,80	6,49 6,75	21,6 21,7	22,2	0,6
Liquid 2, batcn 13	19,70 20,80	7,22 7,53	25,7 25,4	25,6	0,1
Liquid 3, batch 1	20,60 15,90	7,85 5,97	26,7 26,3	27,1	0,6
Liquid 5, batch 44	24,10 14,40	9,31 5,65	27,1 27,5	26,9	0,4

acid, with subsequent titration of the potassium fluorosilicate formed. A determination takes 20-30 min. This method, however, is only suitable for the analysis of monomeric and polymeric ethoxysilanes.

In the work described here, in order to speed up the determination of silicon in silicoorganic compounds, use was made of a method used by us earlier in which various organic and heteroorganic compounds were mineralized with a mixture of chromic and sulfuric acids [1]. The silica formed under these conditions was filtered off[3],

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*The analyses were carried out by L. M. Kharchevnikova.

TABLE 3

Determination of Silicon in Readily Hydrolyzable Silicon-Containing Compounds

Test material	Sample wt., mg	0.1 N HCl used, ml	Si, %		Difference
			found	calc.	
Triethoxysilane	49.55	12.23	17.30	17.10	+ 0.20
$C_6H_{16}O_3Si$	49.70	11.98	16.90		− 0.20
Silicon tetrachloride	41.85	9.93	16.64	16.53	+ 0.11
$SiCl_4$	50.08	12.03	16.85		+ 0.32

dissolved in a concentrated alkali solution, and the silicon subsequently determined titrimetrically using Sir and Komers' method [5]. In the case of the analysis of ethoxysilanes or chlorosilanes (not containing radicals), which are readily hydrolyzed by aqueous solutions of alkali with formation of sodium silicate, silicon determination is further simplified, since there is no need to heat with the acid mixture.

Analytical procedure. An aliquot of the silicoorganic material is placed in a 100 ml short-necked, pear-shaped flask containing 10 ml of concentrated sulfuric acid and 2-3 ml of chromic acid (70 g CrO_3 is dissolved in 100 ml of water) added dropwise with continuous stirring; the mixture is heated for 30 min at 150-160°. The flask is cooled (external cooling with water is not used) and 30-40 ml of water added. The solution obtained is boiled for 5 min at 110-120°. If the solution is not observed to boil at 120°, the flask should be cooled and some water added, after which the solution is heated up again. If, on the other hand, boiling is observed to start below 110°, the solution is evaporated until a temperature of 110-120° is reached. When heating is complete, the solution is cooled to 70-60°, 1-1.5 ml of a 2% gelatin solution added with vigorous stirring, and the solution allowed to stand for 5-10 min for complete coagulation of the silica. The precipitate is filtered off through an ashless, loose filter paper (7 cm) and washed with hot distilled water.

The filter paper plus precipitate are transferred to a polyethylene beaker,* 5-7 ml of a 30% NaOH solution is added until the precipitate has dissolved completely, 5-6 drops of indicator is added,** and the solution neutralized, first of all with hydrochloric acid 1 : 1, and then with hydrochloric acid 1 :10 to a weak acid reaction; the solution obtained is transferred to a conical flask and accurately neutralized with 0.1 N solutions of acid and alkali. At this stage the total volume should not exceed 40-50 ml. The solution is then saturated with neutral potassium chloride in order to prevent hydrolysis of the fluorosilicate, 10 ml of a neutral solution of ammonium fluoride is added,*** followed by 20 ml of 0.1 N hydrochloric acid, and excess of the latter finally titrated with 0.1 N alkali solution.

The method has been checked on a series of individual silicoorganic compounds (Table 1).

Silicon was determined in technical ethylpolysiloxanes by the suggested method. The results of the analyses agree well with the data obtained by the existing method [4] (Table 2).

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*Filtration can be conveniently carried out through a polyethylene funnel and the precipitate dissolved on it in alkali; the solution is collected in this case in a beaker made from nonsilicon material.

**The indicator is made by mixing two solutions; a) a 0.1% alcoholic solution of methyl red; b) to 100 ml of a 0.1% solution of bromocresol green in 20% alcohol is added 0.57 ml of 0.1 N HCl or NaOH. Five parts of solution "a" are mixed with seven parts of solution "b."

***The 1% ammonium fluoride solution is prepared by mixing 20 ml of 25% ammonia solution and 12.5 ml of 40% HF, with cooling, in a polyethylene flask. The mixture obtained is diluted with water to 500 ml and, after rough neutralization, the solution is finally accurately neutralized with standard 0.1 N alkali and acid solutions. The neutrality of the solution thus prepared is checked daily as follows. Twenty ml of 0.1 N hydrochloric acid and 10 ml of the ammonium fluoride solution are titrated with 0.1 N alkali in the presence of 4-5 drops of indicator. When the amount of alkali used differs from the amount of alkali used for titrating 20 ml of acid, the ammonium fluoride solution is neutralized again.

Table 3 contains examples of determination of silicon without preliminary oxidation. In these cases, an aliquot of test material was hydrolyzed in 15% NaOH solution in a polyethylene flask. The solution was neutralized and titrated as described above. We should like to point out that in the case of compounds of this type it is also possible to determine hydrogen linked to silicon, as well as silicon, on one aliquot of sample [7].

SUMMARY

A rapid method for the determination of silicon in silicoorganic compounds has been developed; it is based on their oxidation with a mixture of chromic and sulfuric acids at 150°. The silica thereby formed is filtered off, dissolved in alkali, and converted into fluorosilicate ions in the presence of excess acid, excess of which is back titrated with alkali. A determination takes 1.5 hr. Determination of silicon in compounds which are readily hydrolyzed by aqueous alkali solutions to form silica takes 30 min.

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MICROANALYSIS OF MERCUROORGANIC COMPOUNDS

COMMUNICATION I. DETERMINATION OF CARBON, HYDROGEN, AND MERCURY IN ORGANIC COMPOUNDS NOT CONTAINING HALOGENS

A. I. Lebedeva and E. F. Fedorova

Institute of High Molecular Weight Compounds, Leningrad

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Little attention is given to the elemental microanalysis of mercuroorganic compounds in modern textbooks. The methods in current use for the analysis of such compounds are characterized by their complexity: in most cases a special filling has to be used in the combustion tube; the whole procedure is tiresome and takes a long time. The mercury absorbent used in almost all the current techniques is gold, which, after three to five analyses, has to be regenerated [1-7]. All that has been said above compelled us to develop a more convenient and rapid method for the analysis of mercuroorganic compounds.

First of all we investigated the possibility of determining carbon, hydrogen, and mercury in mercuroorganic compounds on one aliquot. Combustion was carried out in the usual quartz tube; the undecomposed pyrolysis gases were passed over platinum contacts heated to 900°. The mercury vapors were absorbed in a small quartz tube filled with gold turnings, this tube being connected to the combustion tube via a ground joint. The quartz tube was followed by absorbents – anhydrone and askarite. These experiments gave unsatisfactory results.

In the work described here we decided to examine the possibility of carrying out an elemental microanalysis of mercuroorganic compounds without using gold.

We examined the thermal decomposition product of $AgMnO_4$, prepared by Korbl's method [8], as an absorber for mercury. The Korbl catalyst was placed in a quartz apparatus, heated to 105-110°, and connected to the combustion tube via a ground joint. Absorbers filled with anhydrone and askarite followed. Platinum contacts were placed in the combustion tube, which was heated to 900°. We were unable, however, to obtain acceptable results during the analysis of mercuroorganic compounds in such a system. Apparently, the main reason for this lack of success was the use of a ground joint which was not lubricated and was heated in order to expel the mercury vapors. Finally, having abandoned the idea of determining carbon, hydrogen, and mercury simultaneously on one aliquot, we decided to determine carbon and hydrogen on one aliquot and mercury on another.

The carbon and hydrogen were determined in a quartz combustion tube. In the first series of experiments, the platinum contacts were placed in the tube in the zone heated by a large electric oven to 900°. Close to the tip was placed a layer of the thermal decomposition product of $AgMnO_4$, heated to 105-110° with an auxiliary electric oven. The $AgMnO_4$ decomposition product was followed by a layer of silver on pumice. The pumice served to hold back the very small particles of dust carried through from the Korbl catalyst by the oxygen stream. In the very tip of the tube was fitted a lump of silver wire. The results obtained during combustion in a tube filled in this way are given in Table 1.

As is evident from the results given in Table 1, when a tube packed in this way is used, acceptable results are obtained.

TABLE 1

Test material	Sample wt., mg	Found, %		Calc., %		Error, %	
		C	H	C	H	C	H
Diphenyl mercury	6,950	40,64	3,12	40,61	2,84	+0,03	+0,28
$(C_6H_5)_2Hg$	5,080	40,50	3,08			−0,11	+0,24
Dinaphthyl mercury	7,240	52,73	3,24	52,79	3,10	−0,06	+0,14
$(C_{10}H_7)_2Hg$	4,930	52,58	3,09			−0,21	−0,01
Phenyl-p-vinylphenyl mercury	7,540	43,83	3,47	44,15	3,16	−0,32	+0,31
p-$CH_2=CH\cdot C_6H_4HgC_6H_5$	5,490	43,99	3,46			−0,16	+0,30
Phenyl mercury methacrylate	4,720	33,07	3,13	33,10	2,78	−0,03	+0,35
$C_6H_5HgOCOC=CH_2$	8,330	32,99	2,96			−0,11	+0,18
$\vert$ CH_3							
Phenyl mercury acrylate	5,190	30,97	2,63	30,99	2,31	−0,02	+0,32
$C_6H_5HgOCOCH=CH_2$	6,250	30,70	2,42			−0,29	+0,11

TABLE 2

Test material	Sample wt., mg	Found, %		Calc., %		Error, %	
		C	H	C	H	C	H
Dinaphthyl mercury	5,520	52,65	3,16	52,79	3,08	−0,14	+0,08
$(C_{10}H_7)_2Hg$	4,050	52,96	3,12			+0,17	+0,04
Diphenylmercury	5,370	40,65	3,12	40,62	2,84	+0,03	+0,03
$(C_6H_5)_2Hg$	5,120	40,46	3,12			−0,16	−0,16
Phenyl mercury methacrylate	12,020	33,15	2,86	33,10	2,78	+0,05	+0,12
$C_6H_5HgOCOC=CH_2$	7,270	33,22	3,05			+0,08	+0,27
$\vert$ CH_3							
Phenyl mercury acrylate	4,940	31,16	2,43	30,99	2,31	+0,17	+0,12
$C_6H_5HgOCOCH=CH_2$	5,490	30,92	2,59			−0,07	+0,28

In succeeding experiments it was established that combustion of mercuroorganic compounds is readily carried out without using platinum contacts, while the temperature of the electric oven used for heating the thermal decomposition product of $AgMnO_4$ can be lowered to 60°; the other conditions were left unchanged. Absorption of mercury and its oxides was carried out on the same layer (14 cm) of the thermal decomposition product of $AgMnO_4$ as in the previous series of experiments.

Results of experiments on the combustion of mercuroorganic compounds in which platinum contacts were not used, and in which the temperature of the auxiliary oven used for heating the layer of thermal decomposition product of $AgMnO_4$ was 60°, are given in Table 2.

From the results given it is evident that the values obtained for hydrogen are somewhat high, but the error, on an average, is smaller than when the layer of $AgMnO_4$ decomposition product is heated at a higher temperature. When the layer is not heated enough very low results were obtained for hydrogen.

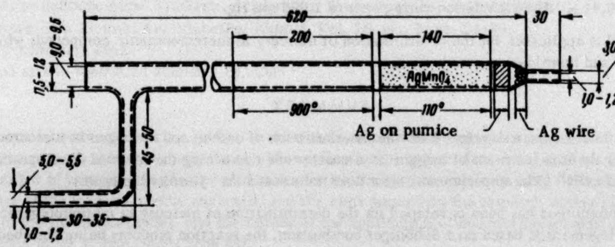
The constant positive error in the hydrogen determination is, presumably, explained by negligible traces of mercury getting into the anhydrone absorber [9].

Korbl's catalyst has the advantage that it is readily available and can be used without regeneration and without replacement for a long time. After 100-120 determinations (for samples containing about 50% mercury) one starts to get low results for hydrogen; this indicates that it is time to replace the catalyst.

The mercury was determined on a separate aliquot of the mercuroorganic compound by burning it in a flask filled with oxygen and then dissolving mercury and its oxides in concentrated nitric acid [10]. The mercury was finally determined titrimetrically. The solution, after appropriate treatment, was titrated with ammonium thiocyanate using ferric alum as indicator [11].

TABLE 3

Test material	Sample wt., mg	Hg found, %	Hg calc., %	Error, %
$(C_6H_5)_2Hg$	5,510	56,17		−0,37
	5,790	56,53	56,54	−0,01
$(C_{10}H_7)_2Hg$	6,010	44,46		+0,36
	3,660	44,11	44,10	−0,01
$P\text{-}C_{14}H_{12}Hg$	3,405	52,32		−0,30
	3,190	52,35	52,68	−0,36
$C_{10}H_{10}HgO_2$	4,390	55,03		−0,26
	6,210	54,86	55,29	−0,43
$C_8H_8HgO_2$	3,950	57,50		−0,02
	4,170	57,60	57,52	+0,08



Tube packed for analysis of organic compounds containing mercury.

The normality of the ammonium thiocyanate was checked against 0.01 N mercuric nitrate which was added to the working solution, i.e., to distilled water containing potassium permanganate, hydrogen peroxide, and an amount of HNO_3 equal to that used for dissolving the mercury and its oxides in each experiment (see experimental section). This technique is a necessary condition for obtaining accurate results [12]. Results of mercury determinations are given in Table 3.

From these results it is clear that the method of determining mercury by combustion in flasks filled with oxygen (Schöniger), followed by titration of mercuric nitrate with ammonium thiocyanate, is reasonably accurate (error ± 0.5%), requires simple apparatus, and is rapid. When combustion by the Schöniger technique is carried out in parallel with determination of carbon and hydrogen, determination of carbon, hydrogen, and mercury takes about 1.5 hr, while, for example, it takes about one hour simply to mineralize an aliquot of a mercuroorganic compound with sulfuric acid [13].

Determination of carbon and hydrogen. The quartz combustion tube (see diagram), after the usual preparation and drying, was packed as follows: into the tip of the tube was placed a lump of silver wire (d = 0.04 mm); next to this was placed a layer of $AgMnO_4$ (about 10 g) heated beforehand in an oxygen stream for two hours at 540°. The layers were separated by packings of calcined asbestos. By means of an auxiliary electric oven the temperature of the $AgMnO_4$ layer was kept within the range 105-110° in the first series of experiments, and within the range 60-65° in the second series. In the first series of experiments, platinum contacts (5 cm) were placed in the zone of the combustion tube heated to 900° by a large electric oven; in the second series of experiments this part of the tube was left empty. A blank run took 25 min. An aliquot of sample (5-8 mg) was placed in a small quartz tube 6.5 cm long and 0.5 cm in diameter. Combustion was carried out in an oxygen stream with a throughput of 18-20 ml/min, and lasted about 15 min. Purging was carried out for 10 min, after which the absorbers (anhydrone and askarite) were removed and weighed 10 and 15 min afterwards, respectively.

Determination of mercury. Reagents. 1. Mercuric nitrate (0.01 N solution). An accurately weighed amount of purified [14] mercury metal (about 1.0030 g) was dissolved by heating in 50 ml of concentrated nitric acid; after cooling, the solution was made up to the mark with distilled water.

2. Ammonium thiocyanate (0.01 N solution). The normality of the ammonium thiocyanate solution was determined as follows: 5 ml of 0.01 N $Hg(NO_3)_2$ solution was pipetted into a flask and 25 ml of twice distilled water, 3 ml of concentrated HNO_3, one drop of a 5% $KMnO_4$ solution, one drop of dilute (about 5%) H_2O_2, and 1 ml of a saturated solution of ferric alum added. The mixture was titrated with 0.01 N NH_4SCN to the appearance of a rose-yellow color.

Experimental procedure. An aliquot of the mercuroorganic compound (3-6 mg) was wrapped up in filter (ashless) paper; the latter was attached to a platinum wire fused into the stopper of the combustion flask and ignited in a 300 ml Erlenmeyer flask filled with oxygen [10, 15-17]. Three ml of concentrated nitric acid had been placed in the flask beforehand. After combustion of the aliquot the flask was allowed to stand for 30 min. The flask was then carefully opened, the stopper and the flask walls were rinsed with twice distilled water, and a 5% $KMnO_4$ solution was added dropwise, with stirring, until a rose color which was stable for five min was obtained. Excess permanganate was destroyed by careful dropwise addition of 5% H_2O_2, and, after addition of 1-1.5 ml of a saturated ferric alum solution, the solution was titrated with 0.01 N NH_4SCN from a microburet to the appearance of a rose-yellow color.

One ml of 0.01 N NH_4SCN solution corresponds to 1.003 mg Hg.

The method is applicable for the determination of mercury in mercuroorganic compounds which do not contain chlorides and bromides.

SUMMARY

A micromethod has been developed for the determination of carbon and hydrogen in mercuroorganic compounds by burning them in a stream of oxygen in a quartz tube containing the thermal decomposition product of $AgMnO_3$ heated to 60°. The experimental error does not exceed the permissible norms.

A rapid micromethod has been developed for the determination of mercury in mercuroorganic compounds not containing halogens; it is based on a Schöniger combustion, the reaction products being absorbed by concentrated HNO_3; the Hg^{2+} formed is finally titrated with 0.01 N NH_4SCN using ferric alum as indicator. The experimental error is ± 0.5%.

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THE USE OF ACETIC ANHYDRIDE AS A DIFFERENTIATING SOLVENT FOR THE SEPARATE ACIDIMETRIC TITRATION OF AMINES, SULFOXIDES, AND AMIDES

N. N. Bezinger, G. D. Gal'pern, and M. A. Abdurakhmanov

Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow

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Nonaqueous solvents which bring out the acid or basic properties of organic compounds which normally appear neutral in aqueous solutions have found wide application in organic functional analysis in the last ten years. The number of nonaqueous solvents used as media for titration is very large and their choice is determined by the character of the materials to be analyzed and the aims pursued by the research worker [1, 2]. A detailed consideration of the theoretical bases and the history of the application of nonaqueous solvents in quantitative analysis are given in N. A. Izmailov's book [3].

Nonaqueous solvents used for acid—base titration can be divided into two types; ones which level, and those that differentiate the strengths of acids and bases. The first type permits determination of the sum of the components in one sample, while the second type permits determination of each component of the test mixture. At present, for materials which are basic in character, the following are used as differentiating solvents: acetonitrile, dioxane, glycols, and ketones. By using a solution of perchloric acid in these solvents it is possible to titrate individually mixtures of alkaloids [4], aliphatic and aromatic, and aliphatic and heterocyclic amines [5]. In the solvents listed, however, it is only possible to titrate those bases whose dissociation constant (in H_2O) is not less than 10^{-11}-10^{-12}.

In the present article a description is given of the use of acetic anhydride as a differentiating solvent for materials which are basic in character.

Acetic anhydride, the arbitrary pH value of which, according to Usanovich [6], lies within the limits of 1 and 3, permits the titration, as bases, of compounds with a dissociation constant (in H_2O) of the order of 10^{-14}-10^{-15}, i.e., compounds which are neutral in aqueous solutions.

Until recently, acetic anhydride has only had limited application as a nonaqueous solvent, mainly as a dehydrating reagent for the titrants and as one of the components during titration in mixed solvents. It has been shown in a number of papers by Soviet and foreign authors that addition of acetic anhydride in amounts of 5-20% with respect to acetic acid, nitromethane, and acetonitrile significantly increases the definition of the titration of weak organic bases [7-9].

The first to use acetic anhydride as a solvent for nonaqueous titration was Gremillion [10], who showed that such materials as diphenylamine [$K_0(H_2O) = 6.3 \cdot 10^{-14}$], urea [$K_0(H_2O) = 1.5 \cdot 10^{-14}$], and thiourea [$K_0(H_2O) = 1.1 \cdot 10^{-15}$], behave as bases in acetic anhydride. In 1958 Wimer published two papers on the titration of carboxylic and phosphoric acid amides [11] and of sulfoxides [12] in an acetic anhydride medium.

We came up against the differentiating action of acetic anhydride during a study of nitrogen bases isolated from petroleum. During this study it was first found that during the potentiometric acidimetric titration of mixtures

Results of Titration of Mixtures of Amines, Sulfoxides, and Amides in Acetic Anhydride by a Solution of 0.1 N $HClO_4$ in Dioxane

Composition	Sample wt., mg	Calculated, mg				Found, mg			
		N-aliphatic amines	N-aromatic and hetero-cyclic amines	S-sulfoxides	N-amides	N-aliphatic amines	N-aromatic and hetero-cyclic amines	S-sulfoxides	N-amides
Dimethyldecylamine*	29,60	2,00		—	—	1,97	—	—	—
Diethylaniline	36,30		3,52	—	—		3,56	—	—
Dimethyldecylamine	39,60	2,68		—	—	2,68		—	—
α-Hydroxyquinoline	29,00	—	2,80	—	—		2,81	—	—
α-Hydroxyquinoline	39,60	—	3,82		—	—	3,82		—
Dibenzylsulfoxide	61,20	—		7,50	—	—		7,50	—
α-Hydroxyquinoline	20,50	—	1,98		—	—	2,01		—
Dibenzylsulfoxide	10,30	—		1,43	—	—		1,41	—
Quinoline	40,00	—	4,33	—		—	4,31	—	
α-Acetonaphthalide	37,00	—		—	2,79	—		—	2,79
1-Ethyl-1,2,3,4-tetrahydroquinoline	33,30	—	2,90	—		—	2,88	—	
β-Acetonaphthalide	30,00	—	—	—	2,26	—	—	—	2,28
Dibenzylsulfoxide	61,80	—	—	8,59		—	—	8,58	
β-Acetonaphthalide	36,60	—	—		2,76	—	—		2,78
Dibenzylsulfoxide	30,50	—	—	4,24		—	—	4,18	
p-Bromoacetanilide	35,20	—	—		2,30	—	—		2,28
Allylbenzylsulfoxide	30,50	—	—	5,23		—	—	5,16	
β-Acetonaphthalide	31,00	—	—		2,34	—	—		2,31
Dibenzylsulfoxide	53,80	—	—	7,48		—	—	7,48	
α-Acetonaphthalide	36,00	—	—		2,71	—	—		2,71
α-Hydroxyquinoline	33,20	—	3,21			—	3,20		
Dibenzylsulfoxide	33,80	—		4,70				4,66	
α-Acetonaphthalide	57,00	—			4,30	—			4,29
1-Ethyl-1,2;3,4-tetrahydroquinoline	31,70	—	2 76				2,71		
Dibenzylsulfoxide	30,70	—		4,27				4,17	
β-Acetonaphthalide	31,80	—			2,40				2,39
Triethylamine	33,00	4,57				4,56			
α-Hydroxyquinoline	43,40		4,19				4,14		
Dibenzylsulfoxide	111,90			15,56				15,50	
β-Acetonaphthalide	30,50				2,29				2,29
Dimethyldecylamine	30,10	2,04				2,02			
1-Ethyl-1,2,3,4-tetrahydroquinoline	69,07		6,07				6,13		
Allylbenzylsulfoxide	63,60			10,92				10,76	
p-Bromoacetanilide	47,70				3,11				3,11

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*All the test materials used for analysis were chemically pure. The dimethyldecylamine contained 6.78% instead of 7.56% N, and was not purified.

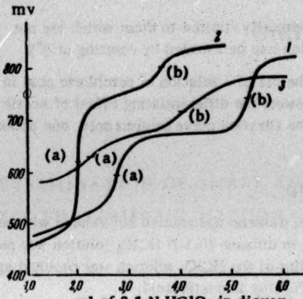

Fig. 1. Titration of two-component mixtures. 1) α-Hydroxyquinoline (a); dibenzylsulfoxide (b), 2) 1-ethyl-1,2,3,4-tetrahydroquinoline (a), β-acetonaphthalide (b); 3) dibenzylsulfoxide (a), α-acetonaphthalide (b).

containing heterocyclic bases (pyridines, quinolines, and thiazoles) and sulfoxides, there were two potential jumps, the first of which corresponded to completion of titration of the base, and the second the completion of titration of the sulfoxides.

The possibility of using acetic anhydride as a differentiating solvent for organic bases was then studied in more detail.

It was shown that it is possible, using acetic anhydride as the medium, to titrate each component of a mixture containing four types of compounds in one aliquot, the mixture consisting of: aliphatic amines, aromatic amines (or heterocyclic bases), sulfoxides, and carboxylic acid amides. The potentiometric titration curves of mixtures containing all four types of compounds exhibit four potential jumps; the first corresponded to completion of titration of the aliphatic amines, the second to aromatic (or heterocyclic) amines, the third to sulfoxides, the fourth to amides. During titration of two- and three-component mixtures, the titration curve has, respectively two and three potential jumps. In order to check the accuracy and reproducibility of the titrations, we made some mixtures containing aliphatic amines—aromatic amines, aliphatic amines—heterocyclic base, heterocyclic base—sulfoxide, sulfoxide—amide, and also mixtures containing three and four components.

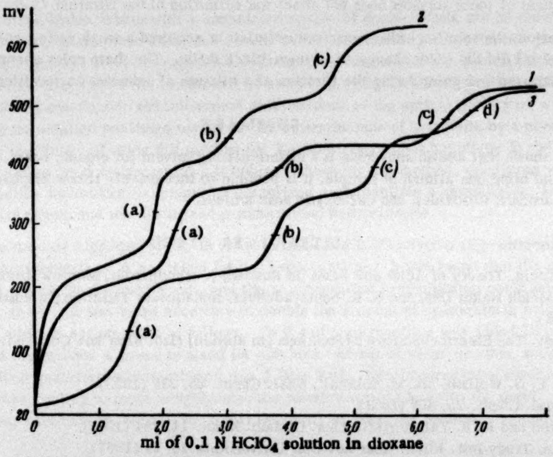

Fig. 2. Titration of three-and four-component mixtures. 1) α-hydroxyquinoline (a), dibenzylsulfoxide (b), α-acetonaphthalide (c); 2) 1-ethyl-1,2,3,4-tetrahydroquinoline (a), dibenzylsulfoxide (b), β-acetonaphthalide (c); 3) dimethyldecylamine (a), 1-ethyl-1,2,3,4-tetrahydroquinoline (b), allylbenzylsulfoxide (c), p-bromoacetaniline (d).

The results obtained are given in the table. The titration curves of some of the mixtures are given in Figs. 1 and 2.

In making up the synthetic mixtures, the choice of amines was naturally limited to those which are not acetylated by acetic anhydride (as Gremillion points out [10], acetylation can be avoided by titrating at 0°).

The titrant used was a solution of perchloric acid in dioxane. The use of a solution of perchloric acid in acetic acid, which behaves as a leveling solvent for the bases tested, lowers the differentiating effect of acetic anhydride; in this case, as a rule, the sum of the bases is titrated and the titration curve exhibits only one potential jump.

EXPERIMENTAL METHOD

Reagents: acetic anhydride, analytical or chemically pure grade; dioxane was treated beforehand with solid NaOH or KOH and distilled over Na metal [13]; 0.1 N or 0.05 N $HClO_4$ in dioxane (0.1 N $HClO_4$ solution was prepared by dissolving 7.5 g of 70% $HClO_4$ in one liter of dioxane). The normality of the $HClO_4$ solution was checked against a standard solution of potassium hydrogen phthalate or methyloctadecylamine in acetic acid.

Titration was carried out using an LP-5 potentiometer. The electrodes used were glass and a saturated calomel electrode connected to the titration vessel through a bridge filled with a saturated solution of LiCl in glacial acetic acid. The solution was stirred during titration with a glass stirrer driven by an electric motor.

Analysis. An aliquot of test mixture containing from 0.0001 to 0.001 M of each component was dissolved in 50-75 ml of acetic anhydride and titrated with a 0.1 N or 0.05 N solution of $HClO_4$ in dioxane, the titrant being added in 0.1 ml portions. When the test material was sparingly soluble in acetic anhydride, it was dissolved in a small amount of nitromethane, dioxane, or chlorobenzene; acetic anhydride was then added and titration carried out. A small amount of these solvents does not affect the definition of the titration.

During titration, the solution either remained colorless or acquired a weak yellow color, and only after adding the last 0.1 ml did the color change to a brown-black shade. The sharp color change could be used for establishing the titration end point during the titration of a mixture of unknown composition.

SUMMARY

It has been shown that acetic anhydride is a differentiating solvent for organic bases. In acetic anhydride as the medium, and using one aliquot of sample, it is possible to successively titrate aliphatic amines, aromatic (or heterocyclic) amines, sulfoxides, and carboxylic acid amides.

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BRIEF COMMUNICATIONS

DETERMINATION OF SMALL AMOUNTS OF BUTADIENE BY A PHOTOMETRIC METHOD

Yu. V. Tsekhanskaya and E. V. Mushkina

State Scientific Research and Planning Institute of the Nitrogen Industry and
the Products of Organic Synthesis, Moscow

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In order to study the dimerization kinetics of butadiene it is necessary to determine small amounts of butadiene in the presence of the butadiene dimer (vinyl-1-cyclohexene-3) and n-hexane or n-heptane. It has been shown [1-6] that diene hydrocarbons with a conjugated system of double bonds can be quantitatively determined by their interaction with aromatic diazo compounds in the presence of polymerization products, and also of paraffin hydrocarbons. Isakova [7-9] has suggested a photometric method for the determination of small amounts of butadiene. The method is based on the interaction of butadiene with diazotized p-nitroaniline hydrochloride with formation of a colored compound, and subsequent measurement of the optical density on a photocolorimeter. Nevertheless, there are no detailed published results on the determination of butadiene by a photometric method, nor information on the possibility of using this method for the determination of butadiene in the presence of its dimerization products and paraffin hydrocarbons. In order to check on this method, conditions were developed for preparing p-nitroaniline hydrochloride, preparing diazotized p-nitroaniline hydrochloride, and carrying out the reaction between butadiene and the diazotized p-nitroaniline hydrochloride.

According to the method suggested [7-9], in order to prepare a 0.2% solution of p-nitroaniline hydrochloride, 6 ml of concentrated hydrochloric acid was taken for 2 g p-nitroaniline. It was found that the amount of hydrochloric acid indicated was obviously insufficient, and the p-nitroaniline hydrochloride could not be dissolved in water even on heating at 60°. It was found necessary to double the amount of hydrochloric acid. The p-nitroaniline hydrochloride solution was prepared as follows. To 2 g of p-nitroaniline was added 12 ml of concentrated hydrochloric acid and the mixture allowed to stand for one hour. 86 ml of water was then added and the solution heated to 60°; it was then quantitatively transferred to a 1 liter flask. Nine hundred ml of water heated to 50° was then added to the flask. After cooling to room temperature, the solution was made up to the mark. On standing, crystals separated from solution; accordingly, before use, it was necessary to filter the necessary amount of solution through filter paper.

Diazotization of the p-nitroaniline hydrochloride was effected at 15-20°, 40 ml of 0.1% sodium nitrite solution being added rapidly with vigorous stirring to 40 ml of the 0.2% p-nitroaniline hydrochloride solution. No color formation should be observed on pouring the solutions together. The solution was prepared immediately prior to the azo coupling reaction with butadiene.

In order to determine butadiene photometrically, a calibration curve was constructed using pure butadiene. Several measurements were carried out on samples kept in sealed ampoules in the case of mixtures of butadiene with n-hexane or n-heptane.

Butadiene regenerated from tetrabromobutane by the action of granulated zinc in an alcoholic medium was used for the work [10]. Tetrabromobutane was prepared by brominating gas containing 90% butadiene and 10% n-butylenes. Butadiene was accurately measured out into the reactor, and also analysis of butadiene from ampoules

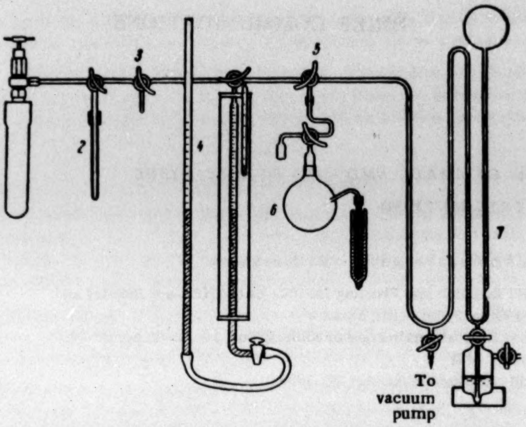

Fig. 1. Setup for measuring and determining small amounts of butadiene.

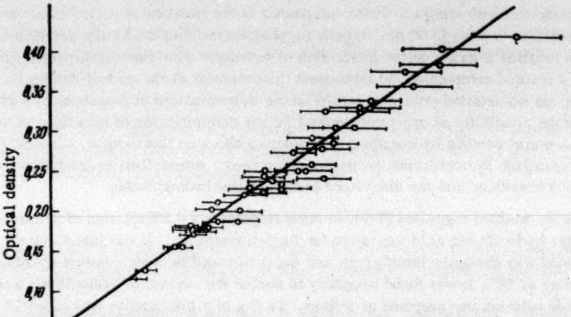

Fig. 2. Relation between optical density of the solution and amount of butadiene.

was carried out in the setup shown in Fig. 1. The setup consisted of a steel autoclave 1 for storing butadiene, a glass ampoule 2, a microburet 4 with a volume of 10 cm³ and scale divisions of 0.02 cm³, and a manometer 7.

Prior to a determination, the microburet was filled with mercury and the air evacuated from the setup by a vacuum pump. An aliquot of butadiene was transferred from the autoclave 1 into the ampoule 2, which was cooled with liquid nitrogen. Subsequently, the ampoule containing the butadiene was unfrozen and the gas passed into the microburet so that a pressure somewhat higher than atmospheric was established in the system. The excess gas pressure in the system was released through tap 3 and the volume of gas in the buret measured, as well as the temperature of the

Determination of Butadiene in the Presence of Butadiene Dimer (temperature 250°)

Duration of reaction, sec × 10^{-3}	Reaction velocity constant, cm^3 $mole^{-1}$-sec^{-1}	Vol. of ampoule, cm^3	Amt. of butadiene, cm^3, 0°, 760 mm Hg		
			before reaction	after reaction	
				calc.	found experimentally
10.65	1.2	1.20	1.37	0.64	0.69
4.68	1.2	2.46	2.26	1.54	1.43
11.77	2.2*	2.48	1.90	0.93	1.00

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*Temperature 260°.

surrounding air and the atmospheric pressure. A glass reactor 6 consisting of a 100 ml round bottom flask with a three way tap was connected to tap 5. When gas contained in an ampoule was to be measured, a flask with a glass outlet tube for connecting it to the opened ampoule was used. The air was evacuated from the reactor and the gas from the buret quantitatively transferred into it by cooling with liquid nitrogen. Accurate measurement of the gas in the reactor was controlled on the basis of the mercury level in the manometer. The gas in the reactor was defrosted and the diazotized p-nitroaniline hydrochloride solution sucked in through the three way tap, this solution having been prepared immediately prior to passing it into the reactor as described above. The reactor was disconnected from the setup and shaken for 10 min at 15-20°. The solution was quantitatively transferred to a 100 ml standard flask and its volume made up to the mark with water; after 10 min the optical density of the yellow solution was measured on an FÉK-M photocolorimeter with a blue filter, using 30 mm cuvettes; the reference solution was distilled water.

For determination of butadiene in its mixtures with n-hexane and n-heptane from sealed ampoules, the contents of the ampoule were frozen with liquid nitrogen; the top of the ampoule was opened and connected via a rubber tube with the side tube of the reactor 6, the ampoule was immersed in liquid nitrogen and the air pumped out of the ampoule and the reactor. The reactor was disconnected from the setup by means of the three way tap 5, and the contents of the ampoule transferred into it quantitatively by cooling the reactor with liquid nitrogen and warming the ampoule. The analytical procedure subsequently followed was the same as that used for the determination of pure butadiene, but with the difference that after making up the volume to the mark in the 100 ml standard flask, the layer of n-hexane or n-heptane was sucked off with a syringe, and the solution filtered through filter paper prior to introducing it into the cuvette.

On the basis of 43 values of the optical density of solutions obtained for amounts of butadiene from 0.53 to 2.9 cm^3 (0°, 760 mm) a calibration curve was constructed within the coordinates optical density–amount of butadiene in cm^3 by the method of least squares (Fig. 2). The mean probable error of a single measurement was ± 7%.

The possibility of using the photometric method for determining butadiene in the presence of the butadiene dimer was checked. For this purpose experiments were carried out on the dimerization of butadiene in the gaseous phase at 250 and 260°. An accurately measured amount of butadiene was sealed in an ampoule. The exact amount of butadiene was introduced into the ampoule by the same method as that used for introducing it into the reactor (Fig. 1, 6), the ampoule being connected to tap 5 instead of the reactor. After measuring out the butadiene into the ampoule, the latter was disconnected from the setup by means of tap 5 and sealed up.

Dimerization was carried out in a thermostat which was a carefully thermally insulated copper block. The heating of the thermostat was automatically controlled by means of a "Siemens" apparatus connected into the circuit of the heating spirals of the thermostat. The temperature was measured directly on the ampoule by means of a double junction chromel-copel thermocouple. The thermostat enabled the temperature to be kept constant up to 270° with an accuracy of ± 0.3°.

The ampoule was immersed in the thermostat which had been brought to the experimental temperature beforehand. The reaction time was counted from the moment when the ampoule was immersed in the thermostat. After completion of the experiment, the reaction products were "quenched" by transferring the ampoule from a thermostat into a metallic ring cooled with liquid nitrogen. During this stage the ampoule was cooled in 3-4 min to 150°, at which temperature dimerization ceases [11]. Butadiene was then determined in the presence of its dimer as described above.

Dimerization of butadiene in the gaseous phase is a homogeneous bimolecular reaction and conforms to an equation of the velocity constants of the second order [11-13]. The rate at which butadiene dimerizes at temperatures from 170 to 390° has been studied in greater detail by Kistakowsky and Ranson [11]. Assuming that the velocity constants of the dimerization of butadiene at 250 and 260° are 1.2 and 2.2 $cm^3 mole^{-1} sec^{-1}$, respectively [11], and knowing the initial butadiene concentration and the reaction time, the final butadiene concentration was calculated by means of a second order equation for the velocity constants (see the table).

A comparison of the final amounts of butadiene, calculated and experimentally determined, indicates that the presence of butadiene dimer does not affect the results of the photometric determination of butadiene.

SUMMARY

A photometric method for the determination of small amounts of butadiene suggested by N. A. Isakova has been checked and modified. It has been shown that it is possible to determine small amounts of butadiene in the presence of butadiene dimer, n-hexane, or n-heptane. The mean probable error of a single determination is ± 7%

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THE USE OF MAGNESIUM METAL IN THE DETERMINATION OF THE ALKALI METALS

P. N. Fedoseev and M. E. Grigorenko

S. O. Makarov Nikolaev Shipbuilding Institute

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On heating organic materials containing halogens, sulfur, nitrogen [1], phosphorus [2], carbon [3], and arsenic [4] with magnesium, halides, sulfides, nitrides, phosphides, and arsenides are formed, respectively. In these compounds nitrogen, sulfur, phosphorus, halogens, and arsenic can be readily determined. Magnesium can be used for qualitative inorganic analysis [5].

The present article is devoted to a description of a method for the quantitative separation of the alkali metals which is based on their reduction with powdered magnesium on heating.

Essentially, the new method for separating and quantitatively estimating the alkali metals reduces to the following: an accurately weighed aliquot of the inorganic material containing alkali metals is mixed with excess powdered magnesium in a stainless steel test tube and the mixture heated at 650-700° for 20-25 min. The air is removed from the tube prior to commencement of the heating. When the reaction is complete, the alkali metals which have been liberated as the free elements are extracted with ethanol and they are subsequently determined titrimetrically or gravimetrically.

TABLE 1

Test material	Alkali metal, %					
	titrimetric method			gravimetric method		
	calc.	found	difference	calc.	found	difference
Na_2SO_4	32,37	32,12	−0,25	43,65	43,52	−0,13
		32,24	−0,13	46,70	46,59	−0,11
Na_3PO_4	42,02	42,16	+0,14	45,35	45,30	−0,05
		41,99	−0,08	28,46	28,38	−0,08
$Na_2B_4O_7 \cdot 10H_2O$	12,05	12,04	−0,01	19,75	19,72	−0,03
		12,06	+0,01	21,74	21,80	+0,06
$NaC_2H_3O_2$	28,02	27,80	−0,22	31,85	31,76	−0,09
		27,98	−0,04	33,07	33,02	−0,05
K_2CrO_4	40,26	40,05	−0,21	49,48	49,40	−0,08
		40,18	−0,06	64,60	64,52	−0,08
$K_2C_2O_4 \cdot H_2O$	42,44	42,34	−0,10	63,01	63,00	−0,01
		42,57	+0,13	56,47	56,40	−0,07
KH_2PO_4	28,73	28,60	−0,13	45,81	45,69	−0,12
		28,72	−0,01	42,70	42,80	+0,10

TABLE 2

Test material	Sample wt.,mg	Alkali metal					
		titrimetric determination			gravimetric determination		
		amt. of 0.05 N acid, ml			calc.	found	difference
		calc.	found	difference			
Total $\left\{\begin{matrix}K_2SO_4\\Na_2CO_3\end{matrix}\right.$	57,60 44,30 101,90	29,90	29,92	—0,02	116,90	116,83	—0,07
Total $\left\{\begin{matrix}Na_2SO_4\\K_2C_2O_4\cdot H_2O\end{matrix}\right.$	52,10 26,30 78,40	20,30	20,36	+0,06	76,97	76,93	—0,04
Total $\left\{\begin{matrix}K_2SO_4\\Na_2SO_4\end{matrix}\right.$	23,50 26,40 49,90	12,80	12,80	—	49,90	49,80	—0,10
Syenite No. PS* 5,05% K	196,30	10,74	10,54	—0,20	41,22	41,25	+0,03
3,18% Na	119,50	7,18	7,10	—0,08	25,35	25,31	—0,04
Syenite No. 271 * 3,75% K	139,80	5,10	5,00	—0,10	20,45	20,40	—0,05
2,00% Na	153,25	5,58	5,55	—0,03	22,27	22,31	+0,04
Syenite No. 1050* 7,33% K	149,05	9,48	9,45	—0,03	25,70	25,74	+0,04
3,02% Na	152,10	9,68	9,60	—0,08	26,25	26,26	+0,01
Syenite No. VS* 8,00% K	114,50	6,88	6,84	—0,04	28,26	28,35	—0,09
2,22% Na	104,10	6,24	6,14	—0,10	26,37	26,30	—0,07

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*Results of analyses carried out at the laboratory of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry.

TABLE 3

Test material	Alkali metals, %					
	titrimetric determination			gravimetric determination		
	calc.	found	difference	calc.	found	difference
Glass 55/134 15,59% Na_2O **	15,59	15,43	—0,16	15,59	15,37	—0,22
	15,59	15,32	—0,27	15,59	15,42	—0,17
Glass 279/747 13,86% Na_2O ** 1,64% K_2O	15,55	15,55	0,00	14,93 *	14,95	+0,02
	15,55	15,40	—0,15	14,93 *	15,12	+0,19
Glass 75/208 15,26% Na_2O **	15,26	15,20	—0,06	15,26	15,19	—0,07
	15,26	15,44	+0,18	15,26	15,00	—0,26
Glass 113/445 15,76% Na_2O **	15,76	15,75	—0,01	15,76	15,87	+0,11
	15,76	15,70	—0,06	15,76	15,86	+0,10
Glass 240/1173 15,15% Na_2O **	15,15	15,02	—0,13	15,15	14,85	—0,30
	15,15	15,08	—0,07	15,15	14,95	—0,20

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*Calculated in terms of Na_2O.

**Standard samples. Results of analyses carried out at the Scientific-Research Glass Institute.

Experimental procedure. The test material (0.05-0.30 g) is introduced into a stainless steel test tube (200 mm long, 10-12 mm in diameter) containing a small amount of powdered magnesium (40-50 mg) Some more magnesium (400 mg) is then introduced into the tube and the contents carefully mixed. In order to avoid undesirable formation of magnesium nitride the air is expelled from the tube either by means of a vacuum pump or by some ether, 0.5-1 ml of which is introduced into the tube. The contents of the tube are then heated for 20-25 min at 650-700°.

Fifty percent alcohol is added in small portions into the cooled tube and the reaction mass broken up with a metal rod. The tube is gently warmed and the solution filtered through a No. 2 porous glass filter. These operations are carried out 10-12 times. The precipitate on the filter is given an additional wash with a small amount of alcohol. The total volume of the wash solution should not exceed 120-150 ml. The alkali metals contained in the filtrate are titrated with 0.1 N sulfuric acid using methyl red as indicator.

In order to determine the alkali metals gravimetrically, the titrated filtrate is evaporated in a beaker to a volume of 5-10 ml; the solution is then transferred to a platinum basin in which it is acidified with 2-3 drops of of concentrated H_2SO_4 and then evaporated to dryness. The alkali metal sulfates are calcined in a muffle oven at 600-650° to constant weight.

Various chemically pure compounds of the alkali metals were analyzed; they included sulfates, phosphates, oxalates (Table 1),etc., as well as mixtures of the compounds indicated (Table 2). In addition, several samples of ores (syenites) containing the alkali metals (Table 2) and glass were analyzed (Table 3).

SUMMARY

A simple, rapid, and accurate method has been developed for the quantitative separation of total alkali metals which is based on their reduction with powdered magnesium. The method does not require any expensive or difficultly available reagents or complex apparatus. A single determination takes 40-45 min.

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*Original Russian pagination. See C. B. translation.

QUANTITATIVE DETERMINATION OF ZINC IN SOILS BY A SPECTROGRAPHIC METHOD

E. A. Pometun and V. I. Boyarova

Institute of Chemistry, Academy of Sciences, Tadzhik SSR, Stalinabad

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The methods which are widely used at present for the spectrographic analysis of metallometric samples [1] are not always satisfactory with respect to sensitivity and accuracy.

We have developed a variant of the method for the direct spectrographic determination of thousandths of a percent of zinc in soils by distilling the zinc from a hollow in a special small electrode. The probable error of a single determination is 8%. The zinc content of the soils is calculated by the three standards method, using a curve relating log I_{Zn}/I_{Cd} to log C.

In contrast to electrodes described in the literature [2-4] the hollow electrode which we used was made from fine spectrographic carbon and was designed to hold 100-150 mg.

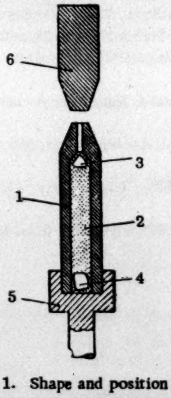

Fig. 1. Shape and position of the electrodes. 1) Electrode; 2) test material; 3) plug of wadding for preventing sputtering of sample; 4) wadding stopper; 5) electrode holder; 6) upper electrode.

The spectra were excited in an activated ac current with a strength of 12 a. The arc served at the same time for heating the lower electrode containing the test sample and for exciting the spectra.

During arc burning, an iodide reducing atmosphere was created in the electrode; the zinc compounds in the solid were converted in this atmosphere into readily volatile zinc iodide. For this purpose the test sample and standards were mixed 1 : 1 with carbon powder containing 10% cadmium iodide, the cadmium in which served as an internal standard at the same time.

The effect of the bulk composition of the samples on the relative intensity of the analytical lines was established. Accordingly, standard powders were prepared on a base similar in composition to that of the test soils. The zinc present in the chosen base was determined by the method of additions [5]. Zinc was added to the standards in the form of its oxide. Samples whose zinc content is fairly accurately known and which at the same time covers the requisite concentration range can also be used as standards.

The hollow electrodes were prepared from normal spectrographic carbon rods with a diameter of not less than 6.3 mm. The total length of the electrode was 25 mm, while the diameter of the hollow was 3.5 mm and the depth 20 mm; the diameter of the opening through which the distilled gases passed was 1 mm. The shape of the electrodes and their position with respect to each other are shown in Fig. 1.

TABLE 1

Analytical lines	Potential		Concentration range of Zn determined, %	Error of a single determination, %
	Excitation of the lines, ev	Ionization of the lines, ev		
ZnI_2 3345.02	7.78	9.39	0.002-0.1	± 8
CdI_2 3133.17	7.76	8.99		
ZnI_2 3282.33	7.78	9.39		
CdI_2 3133.17	7.76	8.99	0.005-0.3	± 8

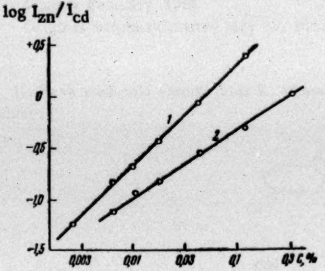

Fig. 2. The relation between the relative intensities of zinc and cadmium lines and the zinc concentration of the soil. 1) ZnI_2 3345.02 and CdI_2 3133.17; 2) ZnI_2 3282.33 and CdI_2 3133.17.

TABLE 2

Zn found, %			
spectrographic method	chemical method	spectrographic method	chemical method
0,12	0,14	0,019	0,020
0,12	0,12	0,021	0,021
0,016	0,018	0,012	0,011
0,014	0,015	0,014	0,013
0,089	0,070	0,018	0,018
0,010	0,012	0,006	0,008
0,015	0,015	0,006	0,004

The spectra of the standards and soils were photographed on "Spectrographic Type I" plates with a sensitivity of 0.8 GOST units, using an ISP-28 average dispersions spectrograph and a slit width of 0.015 mm. The slit was illuminated by means of a three-lens system of condensers, in which the height of the opening of the intermediate diaphragm used for isolating the central section of the arc flame was 1.2 mm.

In order to carry out an analysis, an aliquot of 200 mg of the air-dry soil was mixed with 200 mg of the working mixture (carbon powder and CdI_2 in the proportion of 9 : 1) and carefully ground in a mortar in the presence of alcohol or ether. 100 mg of the mixture obtained was introduced into the hollow of the electrode by means of a funnel and the bottom sealed with a plug of wadding soaked with a solution of ammonium sulfate. The electrode was then firmly fixed in the electrode holder to a depth of 2-3 mm (see Fig. 1). The interelectrode distance was adjusted to 2 mm. The exposure was 30 sec.

The spectrograms were developed under the usual conditions with a standard metal hydroquinone developer.

Zinc was determined on the basis of its most sensitive line ZnI_2 3345.02. The less sensitive line ZnI_2 3282.33 can also be used. The analytical pairs of lines are given in Table 1.

Photometric measurements were made on an MF-2 microphotometer. In order to construct the characteristic curve of the photographic plate the intensities of the iron spectrum were used [5].

Typical calibration curves are shown in Fig. 2. The analytical results taken were the mean of two parallel determinations. In Table 2 are shown the results of parallel determinations of zinc in soils by spectrographic and chemical methods.

The method is in use for the series determinations of zinc in soils during biogeochemical studies. After sufficient practice one worker can carry out 10-12 determinations in a working day, including all preparative work.

SUMMARY

A method has been developed for the direct determination of zinc in soils over the concentration range 0.002-0.1% by using an iodide reducing medium in a small hollow electrode; the probable error of a single determination is ±8%

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PHOTOMETRIC DETERMINATION OF QUADRIVALENT VANADIUM WITH ACID CHROME BLUE K

Yu. V. Morachevskii and I. A. Tserkovnitskaya

A. A. Zhdanov Leningrad University

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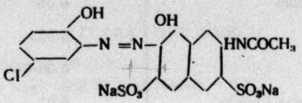
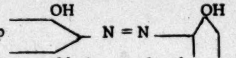
We have used acid chrome blue K, whose formula is given below, for the photometric determination of vanadium:



The presence of the group  led us to expect, in accordance with Kuznetsov's hypothesis [1, 2], that this reagent would give a colored compound with quadrivalent vanadium. In fact such a compound exists at pH 3.6-6, this compound having a maximum light absorption at 590 mμ. The optimum pH range is 4.3–5.3.

The calibration curve was constructed as follows. Two ml of vanadyl sulfate solution in 1 N H_2SO_4 was introduced into a 50 ml standard flask; to this was added an acetate buffer solution (6 ml) and 3 ml of a 0.1% solution of chrome blue K. The solution was diluted to the mark with water. The light absorption was measured on an FÉK-M photocolorimeter using a cuvette with a layer thickness of 50 mm and a green filter.

The color of solutions of the complex conforms to Beer's law over the range 0.01-0.3 μg V/ml. The experimental error is 1-3% (Table 1).

Acid chrome blue K has the highest sensitivity for quadrivalent vanadium (Table 2).

The colored compound of quadrivalent vanadium with acid chrome blue K is stable (the optical density of its solution does not change over a 24 hr period). A state of equilibrium is reached immediately on pouring the solutions together.

The presence of aluminum leads to high results for vanadium. When the amount of aluminum is 25 times that of vanadium, the relative error increases to 10%. Nevertheless, addition of tartaric acid to the solution eliminates interference from aluminum without interfering with the determination. When tartaric acid is present the relative error is not greater than 1.5% even at a ratio of Al : V = 2000 : 1. Molybdenum in ratios up to Mo : V = = 125 : 1 has almost no effect on the vanadium determinations. On increasing the molybdenum further the error becomes appreciable. Tungsten does not interfere at ratios up to W : V = 10 : 1; at higher ratios of tungsten to vanadium, the error becomes appreciable. Under the experimental conditions used, chromium is present in the trivalent state; when the amount of it present is not more than 200 times that of vanadium, it does not interfere.

TABLE 1

V taken, μg	V found, μg	Error	
		absolute	relative
2	2.06	+ 0.06	3.0
6.2	6.1	+ 0.1	1.6
12.5	12.45	− 0.05	0.4

TABLE 2

Reagent	Sensitivity, μg V/ml
Characteristic color of V^{IV}	60
Thoron	0.1
Pyrocatechol	0.05
Stilbazo	0.025
Alizarin	0.02
Acid chrome blue K	0.01

TABLE 3

V found, %	
Phosphotungstate method	With acid chrome blue K
0.50	0.48
0.23	0.22
0.009	0.0087
0.005	0.005

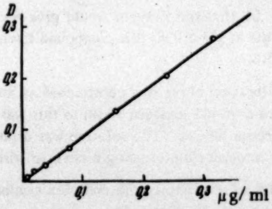


Fig. 1.

When larger amounts of chromium are present, the corresponding amounts of chromium should be added to the reference solution; this naturally assumes a knowledge of its approximate content.

Fluoride, chloride, nitrate, and phosphate ions do not interfere with vanadium determination.

Tartaric and citric acids do not interfere with vanadium determination, but slow down formation of the colored compound of quadrivalent vanadium with acid chrome blue K when the hydroxy acids are introduced prior to the dye. Thus, when citric acid is added to a solution containing 7.9 mg of vanadium, and the acid chrome blue K added afterwards, the color intensity gradually increases, but only reaches a maximum after 24 hr. When, on the other hand, the order of addition is reversed and the dye is added first, followed by the citric acid, the color is established rapidly. Oxalic acid gradually destroys the compound of quadrivalent vanadium with acid chrome blue K. Ascorbic acid does not interfere.

The following technique was used for determining the vanadium content of silicate rocks. An aliquot of 0.1-0.2 g was fused with sodium carbonate and potassium nitrate and the melt leached with water. After filtering off the precipitate of silicic acid, the filtrate was evaporated to the "moist salt" state. The "moist salts" were dissolved in 1 N sulfuric acid. The clear solution was transferred to a 25-50 ml standard flask and made up to the mark with water. To an aliquot of this solution was added 1 ml of 3% ascorbic acid solution and a few drops of formic acid; 6 ml of an acetate buffer was then added, followed by 3 ml of 0.1% acid chrome blue K solution. The volume of the solution was made up to 50 ml. All the reagents, in the same amounts as those used for the test solution, were added to the reference solution. The light absorption was measured on an FÉK-M photocolorimeter using a cuvette with a layer thickness of 50 mm and a green filter.

The results obtained by the method suggested are comparable in accuracy to those obtained by the phosphotungstate method.

The selectivity and sensitivity of the method involving acid chrome blue K is higher, so that it is possible to work with small aliquots.

SUMMARY

It has been shown that it is possible to determine vanadium photometrically with acid chrome blue K.

The compound of quadrivalent vanadium with acid chrome blue K exhibits maximum light absorption at 590 mμ. It is formed in acid solutions; the optimum pH range is 4.3-5.3. The solutions conform to Beer's law for vanadium concentrations within the range 0.01-0.3 μg/ml. The sensitivity of the reaction is 0.01 μg/ml.

The method can be recommended for the determination of small amounts of vanadium in silicate rocks.

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A PHOTOMETRIC METHOD FOR THE DETERMINATION OF RHENIUM IN CATALYSTS

M. A. Ryashentseva and Yu. A. Afanas'eva

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow

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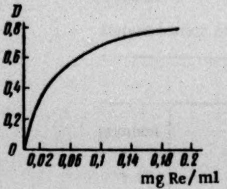
Rhenium is determined quantitatively by a gravimetric method which is based on its precipitation with nitron [1]. Rhenium can be determined photometrically as its compound with thiocyanate [2], α-furildioxime [3], thiourea [4], 2,4-diphenylthiosemicarbazide [5], methyl violet [6], stannous chloride and sodium tellurate [7], etc. Recently, the catalytic properties of rhenium-alumina catalysts have been studied [8]. We have determined rhenium quantitatively in such catalysts by the photometric thiourea method suggested by Ryabchikov and Lazarev [4].

In order to construct a calibration curve, standard solutions of the thiourea complex of rhenium were prepared containing 0.01, 0.02 and then right up to 0.2 mg Re/ml at intervals of 0.02 mg/ml. The standard solutions are prepared as follows. One g of chemically pure rhenium metal is placed in a beaker in which it is treated with 5% HNO_3 by heating until the metal has dissolved completely. The solution is transferred to a 100 ml standard flask in which it is diluted to the mark with water. The solution obtained contains 10 mg rhenium per ml. Standard solutions of the concentrations indicated above are prepared in a series of 50 ml standard flasks; appropriate amounts of the rhenic acid solution are introduced into the flasks, followed by 10 ml of concentrated hydrochloric acid, 10 ml of a 5% aqueous solution of thiourea, and 2 ml of a 20% solution of stannous chloride in concentrated hydrochloric acid; the solutions are finally made up to the mark with water and thoroughly mixed. After one hour, using an FÉK-M photoelectric colorimeter fitted with a No. 3 blue filter, and using cells in which the distance between the working surfaces is 10 mm, the optical density of the standard solutions prepared is measured relative to water. The relation between the optical density of the solutions of the rhenium-thiourea complex and rhenium concentration is shown in the diagram. The curve which we obtained is similar in character to that given in the paper by Ryabchikov and Lazarev [4].

Determination of the Rhenium Content of Rhenium-Alumina

Catalysts	Optical density	Rhenium found	
		mg in 1.00 g sample	%
Before catalysis			
5% Re-Al_2O_3	0.57	60	6
15% Re-Al_2O_3	0.75	160	16
20% Re-Al_2O_3	0.79	200	20
After catalysis			
20% Re-Al_2O_3	0.79	200	20



The relation between the optical density of solutions of the rhenium-thiourea complex and rhenium concentration.

Rhenium is extracted from the catalyst by means of 5% nitric acid; for this purpose 1.00 g of the rhenium-alumina catalyst which has been carefully ground in a mortar is treated in a glass beaker with 25 ml of 5% nitric acid by heating on a boiling water bath for 15 min; the solution is transferred to a 100 ml standard flask and is diluted to the mark with water. The solution is filtered through a No. 3 glass filter. Five ml of the filtered solution is introduced into a 50 ml standard flask; 10 ml of concentrated hydrochloric acid is added, followed by 10 ml of a 5% thiourea solution and 2 ml of a 20% solution of stannous chloride in concentrated hydrochloric acid; the solution is finally made up to the mark with distilled water. The optical density of the solution is measured after one hour, and the rhenium content determined by means of the calibration curve.

An attempt to use 30% hydrogen peroxide instead of nitric acid for extracting the rhenium-alumina catalyst was not successful.

The table contains results obtained during the determination of rhenium in rhenium-alumina catalysts.

SUMMARY

The thiourea photometric method for the determination of rhenium has been used for the determination of the latter in rhenium-alumina catalysts. Metallic rhenium is completely extracted from the rhenium-alumina catalysts by treatment of the latter with 5% nitric acid.

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*Original Russian pagination. See C. B. translation.

A COMPLEXONOMETRIC METHOD FOR THE DETERMINATION OF QUADRIVALENT URANIUM BY MEANS OF THE INDICATOR ARSENAZO I

A. E. Klygin, N. A. Nikol'skaya, N. S. Kolyada,
and D. M. Zavrazhnova

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The method suggested in the present article for the determination of quadrivalent uranium is based on its titration with a solution of sodium ethylenediaminetetraacetate(EDTA-Na), there being no need to remove excess reducing agent.

The minimum pH value (pH_{min}) of 1.15 at which it is possible to titrate a 5×10^{-4} M solution of quadrivalent uranium complexonometrically with an accuracy of down to 0.1% was calculated by means of Yatsimirskii's equation [1] $pH_{min} = 1/4(\Sigma pK_D - pK + 9.30)$, where ΣpK_D is the sum of the indices of the stepwise dissociation constants of ethylenediaminetetraacetic acid ($pK_1 = 2.21$ [2], $pK_2 = 2.77$ [2], $pK_3 = 6.16$ [3], $pK_4 = 10.26$ [3], $\Sigma pK_D = 21.40$) and pK is the index of the instability constant of the ethylenediaminetetraacetate of quadrivalent uranium and is equal to 26.1 [2].

In order to establish the titration end point visually, and in order to increase the selectivity of the method, it is essential to choose an indicator which forms a colored compound with quadrivalent uranium at a pH approximating to pH_{min}. It is known that arsenazo I forms a blue colored compound with thorium, the maximum yield being given at pH 1.9 [4]. By studying the interaction of arsenazo I with uranium, we established that this element also forms a blue colored compound, but the maximum yield in this case is at pH 1.7 ± 0.1. Special experiments showed that during the complexonometric titration of uranium in the presence of arsenazo I, it is only when the pH has the value indicated at the end point that there is observed the clearest change in color from blue to rose. Changes in pH on either side of 1.7 ± 0.1 lead to low results for uranium.

Reduction of a uranyl salt to quadrivalent uranium can be effected by sodium hydrosulfite or by formamidinesulfinic acid [$H_2NC(NH)SO(OH)$], also called thiourea dioxide [5]. Formamidinesulfinic acid is the most convenient to use, since its aqueous solution is more stable, while during the reduction of uranium hardly any sulfur dioxide is evolved. Experiments showed that 0.2 g of formamidinesulfinic acid in 0.25 N sulfuric acid reduces about 200 mg of uranyl on boiling.

The following reagents were used for checking the method:

1. A standard solution of uranyl nitrate containing 7.6 g of uranium per liter. The uranium content was established gravimetrically.

2. EDTA-Na purified by Bleadl and Knight's method [6]. 5×10^{-2} and 2.5×10^{-2} M solutions of EDTA-Na were prepared by taking accurately weighed amounts of the air-dry preparation. The concentration of the solutions was checked against standard thorium nitrate solution [7], while the latter was standardized against uranyl nitrate.

3. Formamidinesulfinic acid was prepared by Fischer and Hieber's method [8] modified slightly by us: a beaker containing 2 liters of 15% hydrogen peroxide was immersed in a cooling mixture (acetone and solid carbon

TABLE 1

Determination of Uranium in Solutions of its Salts in the Presence of Impurities

Taken, mg		No. of uranium determinations, n	Uranium found (mean of n determinations), mg	Mean square error	
uranium	impurities			mg	% (relative)
1,95	—	11	1,88	±0,044	±2,34
7,60	—	11	7,60	±0,099	∓1,30
38,00	—	11	37,95	±0,15	∓0,38
114,00	—	11	114,32	±0,20	±0,18
38,00	6—Fe^{3+}, 5—Al^{3+}	11	37,99	∓0,089	±0,23
38,00	12—Fe^{3+}, 10—Al^{3+}, 500—Na_2SO_4, 500—$NaNO_3$	11	37,99	±0,083	±0,22
38,00	24—Fe^{3+}, 20—Al^{3+}, 1000—Na_2SO_4, 1000—$NaNO_3$	11	38,04	±0,086	±0,23
41,62	30— Tartaric acid	4	41,56	∓0,075	∓0,18
25,15	35— Citric acid	11	25,12	∓0,087	±0,35
25,29	100— Hydroxylamine sulfate	6	25,39	±0,046	±0,18
25,29	100— Hydrazine sulfate	6	25,33	±0,073	±0,29

dioxide). 250 g of finely ground thiourea was added to the contents of the beaker in small portions (1.0-1.5 g) with stirring, care being taken to ensure that the temperature of the liquid in the beaker was within the range −10 to + 10°. The solution plus precipitate obtained were cooled until ice appeared on the beaker walls. The beaker was then withdrawn from the cooling mixture, and, after the ice crystals had disappeared, the precipitate was filtered off through a Buchner funnel; it was washed 2-3 times with water, and dried in the air. The air-dry material is stable on storage. Yield 230 g.

4. Reducing agent solution. Four g of the formamidinesulfinic acid was dissolved in 600 ml of 0.25 N sulfuric acid. The solution can be used for reducing uranium in the course of 24 hr.

5. Arsenazo I solution—0.1% aqueous solution.

6. Thymol blue—0.1% solution in 5% ammonia solution.

During the determination of uranium in solutions of its salts and in the presence of foreign ions, aliquots of the aqueous standard solution of uranyl nitrate were introduced into 300 ml conical flasks and solutions of the impurities, in the amounts indicated in Table 1, added. Thirty ml of the reducing solution was then added to each flask, and the whole heated to the boil and boiled for 5-8 min, the solution being thereby evaporated to a volume of 10-15 ml. Immediately prior to titration, the solutions which had been cooled to room temperature, were diluted with 175 ± 5 ml of distilled water, a pH of 1.7 ± 0.1 being thereby obtained. One ml of arsenazo I solution was then added, and the quadrivalent uranium titrated with EDTA-Na solution with continuous stirring until the color changed from blue to a pure rose.

The method permits determination of 2-115 mg of uranium (Table 1) reliably and with reasonable reproducibility. It is best to establish the titer of the EDTA-Na solution with respect to uranium by means of a standard solution of uranyl nitrate. Al^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Mn^{2+}, Cr^{3+}, Be^{2+}, La^{3+}, Ce^{3+} (in amounts commensurate with that of the uranium) do not interfere with uranium determination; neither does tartaric acid in amounts up to 30 mg, citric in amounts up to 35, sodium sulfate in amounts up to 2 g, sodium nitrate in amounts up to 1 g, nor hydrazine sulfate and hydroxylamine sulfate in amounts up to 100 mg.

Fe^{2+} ions do not interact with EDTA-Na under the conditions we have chosen (pK FeY^{2-} = 14.33, pK FeY^{-} = = 25.1), and, in amounts of 25-30 mg, does not interfere with uranium determination. Nevertheless, when the solution is not stirred adequately during titration in the presence of iron, a localized excess concentration of EDTA-Na may develop (the compound FeY^{-} is partially formed) and the results obtained are high and the reproducibility is poor. Cu^{2+} ions on boiling with a solution of formamidinesulfinic acid are precipitated as Cu_2S; the characteristic

TABLE 2

Comparison of Gravimetric and Complexonometric Determinations of Uranium. The Number of Determinations by the Suggested Method was 11

Test material	Uranium found gravimetrically, % *	Complexonometric method		
		uranium found, % *	Mean square error	
			% absolute *	% (relative)
Uranoso uranic oxide	84.78	84.83	∓ 0.20	∓ 0.24
Uranium tetrafluoride	71.93	71.82	± 0.11	± 0.15
Sodium uranyl acetate	50.82	50.65	± 0.19	± 0.37
Uranium-aluminum alloy	67.96	68.07	∓ 0.16	∓ 0.24
Tributylphosphate solution	34.31	34.41	± 0.06	∓ 0.17
$UO_2(NO_3)_2$	31.79	31.65	± 0.08	± 0.24

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*For solutions, g/liter.

color of copper sulfide interferes with observation of the end point. In the presence of 2-3 mg of copper, determination of uranium becomes impossible if the Cu_2S dissolves in the thiourea. Vanadium salts hinder the quantitative reduction of uranyl, but quadrivalent uranium can still be determined in the presence of 1-2 mg of vanadium if, prior to reduction, 2 g of sodium sulfate is added to the solution and the titration is carried out immediately after reducing the uranium.

Ions which form stable compounds with EDTA-Na (Th^{4+}, Sc^{3+}, In^{3+}, Zr^{4+}, Hf^{4+}) or with quadrivalent uranium (PO_4^{3-}, F^-, $C_2O_4^{2-}$) interfere with the determination. It should be pointed out that oxidation of quadrivalent uranium in the solutions obtained after reduction of uranyl with formamidinesulfinic acid is not observed at room temperature for 8 hr, as long as the solutions do not contain vanadium or they are not diluted with distilled water.

The optimum color change of the indicator at the end point and the highest experimental accuracy are attained on titrating 15-20 mg of uranium. Accordingly, during the analysis of solid materials containing large amounts of uranium it is expedient to carry out determinations on aliquots of the solution obtained after dissolving a large sample. The choice of the dissolution method depends on the composition of the test material. 1.0-0.5 g aliquots of sodium uranyl acetate and uranium oxides are dissolved in 10-20 ml of nitric and 5-15 ml of hydrochloric acid on heating, the solutions being then evaporated to a volume of 3-4 ml. For the analysis of uranium tetrafluoride and alloys of uranium with aluminum, 3-4 ml of sulfuric acid (1 : 1) is added in addition, and the solutions are heated until thick white fumes are given off. The solutions obtained are diluted with water (30-40 ml) and heated to the boil; they are transferred, without filtering, into 100 ml standard flasks, cooled to room temperature, made up to the mark with water, and mixed. An aliquot (15-20 mg of uranium) is transferred to a 300 ml conical flask; 2-3 drops of 0.1% thymol blue is added, followed by ammonia until the color of the indicator changes to orange-yellow (pH 2.5-2.7). Thirty ml of reducing solution is added and the procedure outlined for the determination of uranium in solutions of its salts then followed.

Determination of uranium in kerosene-tributylphosphate solutions was carried out as follows: for uranium contents of 70-10 g/liter, an aliquot (0.5-1.0 ml) was transferred directly into a 300 ml conical flask and 30 ml of the reducing solution added. For uranium contents of 0.3 to 10 g/liter, an aliquot (10-2 ml) was transferred to a 50-75 ml separating funnel, and the uranium extracted with three lots of reducing solution (10 ml in each case), and the re-extracts collected in the same size flask. The determinations were completed as described above.

The results given in Table 2 and other experiments showed that the suggested method permits uranium to be determined reliably and with reasonable accuracy in its oxides, salts, alloys with aluminum, silicon, iron, and beryllium, and also in aqueous and tributylphosphate solutions. In two hours one analyst can carry out 10-12 determinations of uranium in the solutions obtained after decomposing the test material, or after the requisite technological operations.

The authors wish to thank V. A. Golovnya and G. T. Bolotova, who supplied information on the properties of formamidinesulfinic acid and on the reduction conditions for uranium which facilitated the development of the method suggested for the determination of uranium.

SUMMARY

A complexonometric method has been developed for the determination of uranium; it is based on the reduction of uranium to its quadrivalent state by formamidinesulfinic acid with subsequent titration of the solution with EDTA-Na using arsenazo I as indicator.

The method is suitable for the determination of uranium in its salts, oxides, alloys, and in tributylphosphate and other extracts.

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SPECTROGRAPHIC DETERMINATION OF TRACES OF METALS IN HYDROGEN PEROXIDE SOLUTIONS

K. K. Popkov and L. M. Shtifman

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Normal techniques for the spectrographic analysis of solutions [1-2] cannot be used for the determination of traces of metals in hydrogen peroxide solutions, since on introducing such solutions into the flame of an arc or a spark turbulent evolution of oxygen occurs and the foam that is formed short circuits the interelectrode gap. Decomposition of the hydrogen peroxide by boiling it in a flask fitted with a reflux condenser takes from three to eight hours and cannot be recommended.

These difficulties can be avoided by placing a known amount of test solution containing an internal standard on a carbon electrode of special design which is heated to 70-200° (see Fig. 1). The normal type of carbon electrode is turned on a special lathe into the shape of a nail with a concave spherical head. The test solution is placed on this head. A spiral of nichrome wire is heated with a current of 12 v. The electrode is then placed in the support of the spectrograph and combustion is carried out in an ac arc. This method of preparing the sample ensures complete removal of volatile components without destroying the proportion of the metals in the dry residue. Moreover, by evaporating different amounts of test solution with an equal amount of internal standard it is possible to determine the concentration of the metals over a wide range, using for this purpose calibration curves constructed for a comparatively narrow concentration range.

Experimental procedure. Test hydrogen peroxide solution (in 0.2-1 ml lots) containing the internal standard was placed on 2-3 electrodes. The spectra were photographed on an ISP-22 or ISP-28 spectrograph with a PS-39 or DG-1 arc generator. The interelectrode gap was established at a distance of 20 cm from the slit. The current strength of the arc was 3-4 a. The photographs were taken without a condenser. Exposure time was 15 sec. The spectra were measured photometrically on an MF-2 microphotometer. Both reproducing and spectrographic plates were used for recording the spectra. The internal standard was a cobalt sulfate solution with a concentration of 200 mgCo/liter. The most suitable lines were found to be: for the lines Al 2568, Fe 2598, Fe 2599, Cr 2666, Cr 2677, the line Co 2580 was chosen; while for the lines Ni 3002, Ni 3003, Sn 3034, Cu 3247, Al 3092, the line chosen was Co 3044. Calibration curves (Fig. 2) were constructed by preparing five solutions of the chemically pure salts covering the following concentration ranges in terms of the metals: Ni, 10-300 mg/liter; Fe, 10-200 mg per liter; Sn 10-200 mg/liter; Cr, 20-200 mg/liter; Cu, 0.2-3 mg/liter; Al 10-1000 mg/liter. The solutions were acidified with sulfuric and hydrochloric acids.

Because the chosen analytical pairs of lines were not sufficiently homologous, particular attention was given to third element effects and to ensuring that the chosen conditions were rigorously observed.

The presence of Na and K in solution at concentrations less than 1 g/liter does not affect the accuracy and sensitivity of the determination, but at a concentration of 5-10 g/liter of these elements the sensitivity of the determination of all the metals decreases 10-20 times, while the relative error in the determination of Cu, Al, and Cr amounts to 50% and in the determination of Fe to 20-30%. Accordingly, where it is known beforehand that the H_2O_2 solution contains significant amounts of Na and K, analysis of these solutions should be carried out on the basis of standard solutions, to which the appropriate amounts of potassium and sodium salts have been added. Organic

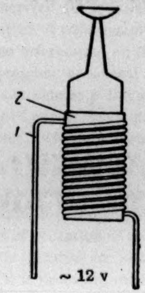

Fig. 1. Carbon electrode with heater. 1) Nichrome wire spiral, diameter 0.5 mm; 2) mica insulation.

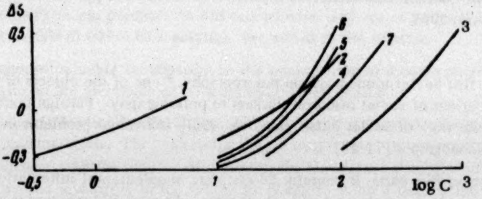

Fig. 2. Calibration curves. 1) Cu 3247; 2) Al 3092; 3) Al 2568; 4) Sn 3034; 5) Fe 2599; 6) Ni 3002; 7) Cr 2666. The difference in blackening $\Delta S = S_x - S_{Co}$ is plotted along the ordinate.

compounds are almost completely removed after placing the samples on the electrode and heating them to 300-400° in the same nichrome spiral. Incompletely burnt organic materials lower the sensitivity of the determination of impurities, on an average, by one order.

The method described permits determination of from 0.1 to 1000 mg/liter of iron, nickel, chromium, tin copper, and aluminum in hydrogen peroxide solutions. The relative mean square arithmetic error is 10-15%. During analysis of solutions containing less than 0.5 g/liter of K and Na, the relative error drops to 5%. Three parallel determinations are carried out and the mean taken. Analysis of one sample takes about one hour.

SUMMARY

A spectrographic method is described for the determination of nickel, iron, tin, chromium, copper, and aluminum in hydrogen peroxide solutions; it covers the range 0.2-3 mg/liter in the case of copper, and 10-1000 mg/liter for the remaining elements. The hydrogen peroxide is evaporated on a heated graphite electrode of special design. The part of the electrode containing the dry residue is completely burnt in an ac arc.

Cobalt lines are used as the internal standard. Cobalt is introduced into the hydrogen peroxide beforehand.

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REVIEW AND BIBLIOGRAPHY

T. A. KRYUKOVA, S. I. SINYAKOVA, AND T. V. AREF'EVA

POLAROGRAPHIC ANALYSIS. Goskhimizdat, 1959, 772 pages.
5,000 printed. Price 34 rubles, 50 kopecks.

Reviewed by A. G. Stromberg

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The book is the first Soviet monograph on polarography,* one of the objects of this book being the bringing together of the contributions of Soviet research workers to polarography. Foreign textbooks [1-10] do not deal in sufficient detail with the work of Soviet polarographists. Only individual problems in polarography have been considered in Russian monographs [11-14]

The book consists of five parts; it contains 26 chapters, supplemental information, and an appendix. References to the literature are given at the end of each chapter. About 2,500 references are given. At the beginning of the book a list is given of the basic textbooks and reviews on polarography and its individual branches.

The first part (Chapters I-IV, 165 pp., 504 references) is devoted to a consideration of the theoretical and experimental bases of polarography.

Modern ideas and rules of electrochemistry are considered in the first chapter (the double electrical layer, null charge potential, the theory of concentration polarization and convection diffusion, the effect of potential on the adsorption of surface-actice materials on the mercury electrode, the concept of ψ' potentials, etc.). Unfortunately, this chapter does not deal with modern ideas on the kinetics of electrode processes developed by A. N. Frumkin, et al. (the concept of the exchange current, transport coefficient, the slow discharge – ionization theory, etc.).

The second chapter is devoted to an exposition of the fundamental theoretical basis of polarography. Here is treated in particular detail, and this is very valuable, the theory of maxima on polarographic waves and the mechanism of the inhibition of tangential movements of mercury by surface-active materials, which has been developed almost exclusively by Soviet workers, in particular, by one of the authors of the book (T. A. Kryukova). These questions are treated incompletely and inaccurately in foreign monographs. Fairly detailed consideration is also given in this chapter to the theory of the effect of various factors on the diffusion current, the theory of the charge current, the theory of catalytic waves, and some other theoretical questions. About 400 references are given to the literature on polarographic theory.

The introduction of more detailed consideration of some theoretical problems in polarography (derivation of equation for the diffusion current and for polarographic maxima) into the "Supplement" at the end of the book is a good idea.

There are, however, serious gaps in the exposition of the theory of polarography. Completely inadequate attention has been given to the theory of reversible and irreversible polarographic waves. Equations for various reversible waves have not been derived (in solutions of simple and complex ions, during overcharging of ions, for organic materials). The application of polarography to the study of complex compounds is treated very incompletely. In particular, there is no information on De Ford and Hume's method for calculating the composition and instability constants in the presence of several equilibrium complexes in solution. Almost nothing is said about the theory of irreversible and kinetic polarographic waves, a theory which has been considered in detail in the last ten years in a number of papers (see,e.g.,[10]). It is true to say, however, that these questions have received some attention in chapter XXIV (amalgam polarography).

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*The importance attached to polarography in recent years is illustrated by the award of a Nobel prize for chemistry to the famous Czech scientist, Ya. Heyrovsky, who discovered and developed the polarographic method.

The third chapter contains a lot of new and original material on the effect of various factors on the functioning of the dropping mercury electrode. Valuable information is also given about other electrodes which have been finding ever wider application in polarography. The drawback of this chapter is the absence of a clear distinction between the two main types of operation of the dropping mercury electeode: 1) in practical analytical work, in which surface-active materials (gelatin) are added; and 2) in certain special cases which are encountered in physicochemical studies where it is necessary to obtain a normal diffusion current on a dropping mercury electrode in the complete absence of any surface-active materials. Most of the complications which are met during work with a dropping mercury electrode and which are noted in this chapter (richly illustrated with experimental material obtained by the author) relate precisely to this second case and are of no great importance in practical work when surface active materials (0.002-0.01% gelatin) are added to the solution.

The fourth chapter contains valuable information on the construction of modern polarographs and polarographic electrolyzers, and also on the technique of polarographic investigation.

The second part of the book (Chapters V-XIII, 225 pp., 511 references) is devoted to the application of polarography to the analysis of inorganic materials. The material on the polarography of the various elements is systematized into eight chapters, in accordance with the number of groups in the Mendeleev periodic system. The polarography of anions and molecules is treated separately in the thirteenth chapter. After a description of the polarographic properties of a given element in various supporting electrolytes, determination of this element in various technical and natural materials is discussed. First of all a general description of the technique is given, the requisite reagents and solutions are then listed, and finally the experimental procedure is described in detail. This part of the book is a very useful practical textbook for workers in chemical laboratories who use polarography for the analysis of various materials. Soviet literature on the polarography of inorganic compounds (up to 1955-1956) is very fully treated in this section, and the work of foreign workers is also covered. It should be pointed out that the authors of this part of the book (S. I. Sinyakova and T. V. Aref'eva) have themselves many years' experience in developing polarographic techniques for the analysis of mineral raw materials and nonferrous mineralogical products.

The use of polarography in the analysis of organic compounds is the subject of the third part of the monograph (Chapters XIV-XVIII , 108 pp., 296 references). After a discussion of some general questions in the polarography of organic compounds (chapter XIV), the four succeeding chapters are devoted to the polarography of various groups of organic compounds, on the same plan as that adopted for polarographic compounds. Nevertheless, the literature on the polarography of organic compounds* (particularly foreign) is treated far less fully than that on the polarography of inorganic compounds.

The fourth section of the book (Chapters XIX XXII, 67 pp., 125 references) considers the general principles (Chapter XIX) and individual techniques of amperometric titration. Recently O. A. Songina's monograph on amperometric titration [11] was published, and the literature on this question was dealt with much more fully there (427 references).

The fifth part of the book (Chapters XXIII-XXVI, 32 pp., 84 references) is devoted to various other questions in polarographic analysis: adsorption analysis, amalgam polarography, derivative, differential, and oscillographic polarography. These special divisions of polarography have been finding increasing significance in recent years. Thus, amalgam polarography on a stationary mercury drop at a constantly changing potential and oscillographic polarography permit determination of some elements at concentrations of 10^{-7}-10^{-8} M. It is a pity therefore that the authors of the monograph have given such little space to these new branches of polarography.

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*To have an idea of the volume of literature on the polarography of organic compounds, one can cite Wawzonek's review [15], in which 500 references are given covering three years (1955-1957).

Tables are given in the appendix which contain the half-wave potentials of inorganic compounds (about 1000 values) and organic compounds (about 800 values). Opposite each half-wave potential is given the literature reference, a list of which is given at the end of the tables. (Bibliography, 636 references). Of great value are the polarographic spectra of the elements in fifteen supporting electrolytes (pp. 726-727). These spectra can be used for choosing the requisite supporting electrolyte for the analysis of a given mixture of elements.

It can be said that the authors have compiled a valuable book which can serve as a means for making one's acquaintance with the theoretical bases of polarography and as a textbook in carrying out polarographic determinations during the analysis of complex inorganic and organic materials. It only remains to deplore the fact that such a small edition has been published (5,000); this will not be enough to satisfy the large demand there will be for it.

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CURRENT EVENTS

CONFERENCE ON KINETIC METHODS OF ANALYSIS

(JUNE 14-16, 1960, Ivanovo)

V. P. Vasil'ev, V. D. Korableva, and K. B. Yatsimirskii

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 1, p. 118,
January-February, 1961

At the conference on kinetic methods of analysis, 16 reports were presented by workers at the Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR; the Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian SSR; Moscow, Kiev, and Dnepropetrovsk Universities; the Ivanovo Chemico-Technological Institute; and the Institute of Chemical Reagents (IREA). Representatives of a number of colleges, scientific-research institutes and factory laboratories, as well as chemists from Ivanovo, took part in the work of the conference.

The following reports were read and discussed: I. P. Alimarin and Yu. V. Yakovlev, "The Possibilities of Modern Methods for the Determination of Ultra Small Amounts of Impurities in Super Pure Materials"; K. B. Yatsimirskii, "The Modern State and Perspectives of the Development of Kinetic Methods of Analysis"; A. K. Babko and L. V. Markova, "The Photometric Determination of Micro Amounts of Sulfides and Sulfur in Metals on the Basis of their Catalytic Action on the Iodine-Azide Reaction"; B. E. Reznik and N. V. Pchelkin, "The Photometric Determination of Copper and Molybdenum on the Basis of their Catalytic Action"; B. E. Reznik, G. M. Ganzburg, and N. A. Bednyak, "A Study of the Catalytic Action of Certain Transition Elements on the Reduction of Molybdenum by Thiocyanate"; R. P. Pantaler, "A New Kinetic Method for the Determination of Traces of Tungsten and Molybdenum"; L. T. Bugaenko, "The Use of the Kinetic Method of Analysis in Radiation-Chemical Studies"; S. I. Sinyakova, "A Review of the Use of Kinetic (Catalytic) Currents in Polarography for the Determination of very Small Amounts of a Number of Elements"; K. B. Yatsimirskii and L. I. Budarin, "Determination of Equilibrium Constants in Systems Involving Complex Formation on the Basis of a Study of Catalytic Polarographic Currents"; V. I. Kuznetsov and E. S. Ul'yanova, "Radiation-Kinetic Determination of Polonium"; L. I. Budarin and K. E. Prik, "New Types of Apparatus for Kinetic Methods of Analysis"; M. N. Orlova, "Kinetic Methods of Determining Silver in Solution"; A. K. Babko and N. M. Lukovskaya, "The Effect of Complexing Agents on the Catalysis of Chemiluminescence Reactions"; L. P. Raizman, "A Study of Complex Formation between Zirconium and Organic Acid Anions by a Kinetic Method"; K. E. Prik, "The Application of the Kinetic Method to the Study of Complex Formation of Sexivalent Molybdenum in Solution"; and M. B. Shustova, "The Determination of Vanadium in Titanium Metal."

Lively exchanges of opinion followed the reports. The conference showed that work on kinetic methods of analysis is now being successfully carried out in many cities (Moscow, Kiev, Ivanovo, Dnepropetrovsk, Khar'kov, and Odessa). The most important lines followed by these studies were indicated. It was pointed out that it is necessary, on the basis of results already obtained, to go over to developing actual analytical techniques for practical use. One of the most important lines of research is to clarify the mechanisms of the catalytic reactions in use; a fuller study of their kinetics is possible. Of very great interest is the search for the connection between the various physicochemical characteristics of catalyst particles and their catalytic activity. The existence of a profound mutual connection between the problem of complex formation and the reaction kinetics in solution was demonstrated at the conference.

In order to carry research further in the field of kinetic methods of analysis it is necessary to develop new types of apparatus and to bring them into production; to issue special samples and standard materials whose content of micro impurities has been definitely established; reagents of particularly high purity are also required. It is desirable that reviews and monographs be published on kinetic methods, and that the links between research workers in this field, both in this country and beyond it, be strengthened.

FIFTH CONFERENCE ON THE ANALYSIS OF THE NOBLE METALS

(SEPTEMBER 20-23, 1960, Novosibirsk)

O. E. Zvyagintsev

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 1, p. 119,
January-February, 1961

The Fifth Conference on the Analysis of the Noble Metals was convened by the Institute of Inorganic Chemistry of the Siberian Branch of the Academy of Sciences, USSR, and the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, in conjunction with the Ministry of Finance, USSR, and the Council of National Economy of the Novosibirsk Economic Region. One hundred and twenty eight participated in the conference; they came from 18 cities in the USSR and represented 42 organizations: scientific-research institutes, higher education establishments, industrial enterprises, and state institutions. The conference heard and discussed 30 reports presented both by scientific workers and by factory workers and demonstrated the close connection between scientific and engineering forces.

K. B. Yatsimirskii (Ivanovo) gave a review on "The Use of Kinetic Methods for the Determination of the Noble Metals." In this report, in conjunction with M. N. Orlova, he gave an account of the concrete application of the measurement of the rates of certain reactions for determination of gold and silver in solution.

I. T. Filenko and I. Ya. Baulina reported on an approximate method for the determination of the composition of gold native ores without damaging them. N. S. Balandina and G. G. Kalyuzhina (Novosibirsk) reported on some techniques which they have developed for separating impurities from normally refined gold, and for preparing very pure gold by ether extraction. The total amount of impurities in such gold is not higher than 0.0001%.

V. P. Khvostova from the firm of V. M. Peshkova and V. I. Shlenskaya (Moscow) reported on the analytical use of the reaction of palladium with potassium thiocyanate, and its study by a spectrophotometric method.

A. T. Pilipenko and I. P. Sereda reported on the use of selenourea for the colorimetric determination of osmium and rhenium without their preliminary separation.

V. N. Alyanchikova, L. V. Karpova, A. D. Dut'ko, and G. V. Ryseva (Krasnoyarsk) reported on the use of spectrophotometry, photocolorimetry, and amperometry for the determination of platinum, rhodium, iridium, and ruthenium without separating them.

Three reports were devoted to spectrographic analysis, those of: V. L. Ginzburg (Moscow), "Spectrographic Analysis of Tellurium for its Content of Noble Metals"; V. P. Khrapai (Novosibirsk), "Spectrographic Methods of Analysis in the Determination of Impurities in High Purity Gold"; A. D. Dut'ko and N. I. Pankratova (Krasnoyarsk), "Spectrographic Analysis of Platinum, Palladium, and Ruthenium of High Purity."

Several reports were given by workers in the analytical laboratory of noble metals in the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR (Moscow), on work carried out under the direction of N. K. Pshenitsyn: K. A. Gladyshevskaya and L. M. Ryakhova, "The Separation of Rhodium and Iridium by Ion Exchange using the Complex Compounds of these Metals with Pyridine"; N. A. Ezerskaya, "New Polarographic and Amperometric Methods for the Determination of Ruthenium in the Form of Sodium Hexachlororuthenate"; N. N. Chalisova, "Methods of Separating Selenium and Tellurium during the Analytical Separation and Determination of Platinum Group Methods"; S. I. Ginzburg, "New Methods for the Determination of Noble Metals in Copper and Nickel Slags and in Platinum Concentrates."

A group of research workers from Kishinev–M. G. Bardin, et al.–gave a report on the polarographic determination of noble metals on a rotating platinum microdisc electrode.

V. A. Oborinskaya (Novosibirsk) reported on the use of an electrometric method for the analysis of gold-silver alloys using a chromate-silver electrode.

Two reports were given by representatives of the Noril'sk Mining-Metallurgical Combine: V. S. Belokopytov gave a review of assay-spectrographic methods of analysis, while Comrade Kashlinskaya gave a report on the chemical methods used in the combine.

The report of N. N. Maslenitskii and A. V. Polievskii (Leningrad) dealt with assay analysis for gold and silver in materials containing large amounts of iron and chromium oxides.

S. M. Anisimov, A. P. Osipov, and A. I. Chernova (Ordzhonikidze) reported on methods they have developed for the determination of small amounts of rhodium, ruthenium, and iridium by means of assay melts, and on further analysis by spectrographic and photocolorimetric methods.

A. S. Artemov gave some brief information on the work of the assay group of the central laboratory of the Irtyshskii Polymetallic Combine.

I. D. Fridman (Moscow) dwelt on the loss of gold and silver in cemented drops, which is of importance for assay laboratories.

The last report to be read was that of S. K. Shabarin (Moscow): "Notes on the History of the Art of Assaying in Russia (XVI-XIX centuries)."

The conference adopted a resolution which indicated the main lines of further work on the analysis of noble metals. It was particularly emphasized that it is necessary to renew work on sampling technique on materials containing noble metals, and on the mechanization and automation of sampling processes.

It was decided to hold the next (sixth) conference on the analysis of the noble metals in Krasnoyarsk in 1963.

YU. A. KLYACHKO
(On his Fiftieth Birthday)

Recently Professor Yu. A. Klyachko celebrated his fiftieth birthday.

Yurii Arkad'evich Klyachko started his scientific and teaching activity at the beginning of the thirties, during the beginning and turbulent development of Russian science and industry. Until 1939 Yu. A. Klyachko worked in a factory and at the same time carried on with his teaching work. Much of his work on colloidal phenomena in metals relates to this period. In the field of analytical chemistry Yurii Arkad'evich gave most of his attention to developing methods for the determination of gases and inclusions in light metals.

In the post war period, Yu. A. Klyyachko developed the questions of the application of the periodic law in analytical chemistry, and the theory of precipitation formation.

Much of the work of Yurii Arkad'evich has been devoted to the physicochemical study of processes which occur during the analysis of gases in metals, and also during the anode dissolution of alloys, for the purpose of their phase analysis. Yu. A. Klyachko has devoted particular attention to the origin and behavior of hydrogen in metals. He has contributed a great deal to the development of analytical apparatus.

Yurii Arkad'evich has written the following books: "Oxidimetry" (in collaboration with L. V. Timofeev); "A Course in Qualitative Analysis" (in collaboration with S. A. Shapiro); and "The Analysis of Gases and Inclusions in Steel."

Yu. A. Klyachko has always been distinguished by intense energy and his huge capacity for work. In 1933 he took an active part in editing the journal "Zavodskaya Laboratoriya"; in the D. I. Mendeleev All-Union Chemical Society; the Commission on Analytical Chemistry, Academy of Sciences, USSR; and in the work of the editorial boards of a number of journals and publishing houses.

He has written more than 150 scientific papers.

We wish Yu. A. Klyachko new creative successes, health, and many years of fruitful labor.

The Commission on Analytical Chemistry
Academy of Sciences, USSR

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

INCREASING THE SENSITIVITY OF DETERMINING ELEMENTS IN A FLAME

V. I. Lebedev and E. E. Vainshtein

V. I. Vernadskii Institute of Geochemistry and
Analytical Chemistry, Academy of Sciences,
USSR, Moscow

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Despite the fairly high sensitivity of the flame photometric method, particularly for the determination of relatively readily excited elements, and the widespread use of this method in modern analytical chemistry, practical demands, in particular, those of geochemistry and chemical technology, require that the sensitivity of the method be increased further, and that it should be applicable to the determination of a larger number of elements. Since the sensitivity of the method is determined finally by the ratio of the value of the useful signal in the recording setup to the background (or, more accurately, by the fluctuations in the background*), in principle, there are two possible methods of solving this problem. The first of these methods—increasing the relative (compared with the background) intensity of the useful signal—is related to the presence of a minimum amount of the test element in the test material. This can be achieved by increasing the flame temperature and adopting a number of measures relating to preparing and introducing the test solutions into the flame, measures which taken together would increase the number of atoms emitting radiation per unit time in the source. The second method would be, in essence, to decrease the background and increase its stability, by using more advanced spectral equipment characterized by a higher resolving capacity, and to improve the system used for recording the intensity of the analytical lines of the test element. Under such conditions one would expect an increase in the accuracy and selectivity of the determination as well.

Many papers have been published recently describing work carried out along both these lines: the use of flames with higher temperatures [2, 3], and the use of more advanced optical apparatus and apparatus for recording the spectra [4, 5].

The present article is devoted to results of studies carried out in our laboratory.

Combined Sources of Spectra Excitation. One of the possible ways of increasing the source temperature for carrying out quantitative spectrographic analysis in a flame would be to set up combined sources, flame-spark or flame-arc. The possibility of increasing the sensitivity of the spectrographic determination of certain elements by means of a flame-spark source has already been pointed out [6,7]. Nevertheless, the lack of published information on the properties of the first of these sources, coupled with the fact that the second source has not been studied at all, necessitated more systematic studies. The arrangement of both the spectra excitation sources studied is shown schematically in Fig. 1 (a and b). The ac arc or the spark fed from a DG-1 generator, were fixed horizontally and were ignited crosswise through the flame at a height of 10-15 mm above the top of the burner. Copper electrodes 7 mm in diameter were used. Carbon electrodes are unsuitable because of a strong increase in

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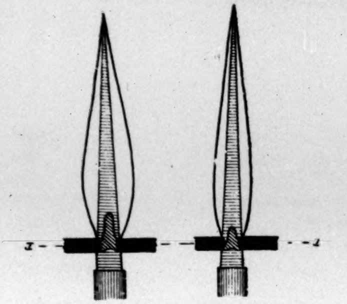
*On this basis, Al'kemade [1] for example, suggests that the sensitivity of the method should be regarded as that concentration of the test element which gives a deviation (reading) in the recording apparatus equal to the experimental error in reading the scale.



a b

Fig. 1.Combined excitation sources. a) Flame–arc; b) flame–spark.

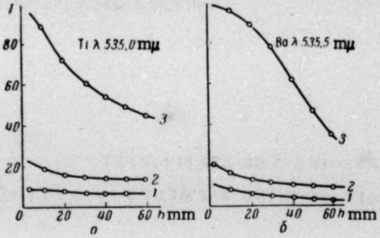


Fig. 2. The relation between the intensity of the analytical lines of Tl (a) and Ba (b) and the height (h) above the level X – X (Fig. 1) in different sources. 1) Flame; 2) flame–spark; 3) flame–arc.

background. The analytical gap was 6-9 mm. The current supplied to the arc was 3 amp, while that supplied to the spark was 2 amp. The spectrographic apparatus used was an ISP-51 spectrograph, the camera of which had F = 270. The spectra were recorded photographically ("Infra-760" and "Isochrome" plates with a sensitivity of 45 GOST units), and by means of a photoelectric setup* with a photomultiplier using an integrating scheme similar to that described by other authors.

In Fig. 2 are shown some of the curves obtained in this way; they illustrate the relation between the intensities of the analytical lines of various elements, and the height of the part of the flame being photometrically measured above the level at which the arc or the spark of the combined source is located. The curves shown are those of the analytical lines Ba (λ = 553.5 mμ) and Tl (λ = 535.0 mμ). Curves similar in appearance were also obtained for other elements. (Ga, In, La, and Yb). As is evident, the intensity of the analytical lines of the elements in a combined source is considerably greater than that in a flame. At the same time, the efficiency of a flame–arc source is higher in all cases (the intensity of the analytical lines is higher) than that of the second combined source. In the case of Ba the line intensity in a flame–spark source is 2-6 times that in a flame, while the line intensity in a flame–arc source is 6-25 times greater. The corresponding values for Tl are 1.7-2.5 and 5-9 times respectively.

Unfortunately, in parallel with the increase in the intensity of the analytical lines of the elements in the combined sources, there is also a strong increase in the background intensity, which, on using a photometric method of recording, as a rule**, makes it impossible to use the advantages indicated above of the combined sources (Fig. 3). In order to overcome this difficulty it would be necessary to use a discriminating scheme of recording the spectra. The simplest prototype of such a scheme would be, for example, a photographic plate whose sensitivity with respect to a weak background would be much less than its sensitivity to the most intense spectral lines. In this case, the combined sources of spectra excitation described above for increasing the sensitivity of the determination of certain elements would prove efficient enough used as they are.

In conclusion, we should like to point out that the combination of a flame with a higher temperature source – an ac arc or a spark – leads to an increase in the stability of these sources themselves (this is clearly shown in Fig. 4). It is possible that this could be used in spectrochemical research for developing an efficient method for introducing samples into the inter-electrode space of high temperature sources. Such a technique, which is an original analog of the well-known variants of the "spilling" method, in certain cases could, presumably, make it possible to increase the accuracy of the spectral determination of the elements.

*For a more detailed description of the operation of the photoelectric setup, see the following section of the present article.

**In the case of some elements (e.g., Ba), however, it is possible to find regions in the flame of the combined sources, for which $I_{line}/I_{background}$ approaches the value characteristic of a flame. In such cases, the significantly higher absolute intensity of the analytical line of the element in a combined source can be used for analytical purposes.

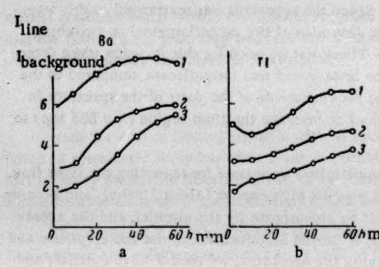


Fig. 3. The relation between the ratio $I_{line}/I_{background}$ and h for Ba (a) and Tl (b) in different sources. 1) Flame; 2) flame–spark; 3) flame–arc.

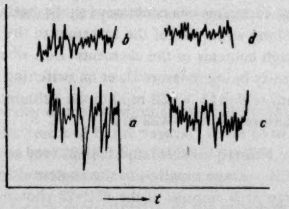


Fig. 4. The change in the intensity of the line Sr 460.7 mμ with time in different sources. a) Arc; b) flame–arc; c) spark; d) flame–spark (recorded on an EPP-instrument).

Recording Flame Spectrophotometer. With the aim of studying the second approach mentioned above for increasing the sensitivity of the determination of elements in a flame, we assembled a recording spectrophotometer. The setup is shown schematically in Fig. 5. It is assembled in the main from ready made units turned out by Russian industry. An ISP-51 spectrograph is used as the spectral apparatus. The FEP-1 recorder is used for taking and recording the spectra; it is designed for recording combination scattering spectra in the wavelength range 380-600 mμ.

The linear dispersion of the setup for λ = 4713 A is 32 A/mm, which is close to the linear dispersion of the ISP-51 apparatus fitted with a camera with F = 270 mm. The maximum amplification factor of the amplifier is 10^8. The chart tape speed could be varied from 60 to 9600 mm/hr. The run-down time of the carriage in the recording potentiometer of the instrument we used was 2.5 sec.

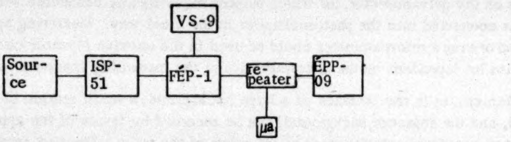


Fig. 5. Schematic diagram of the recording flame spectrophotometer.

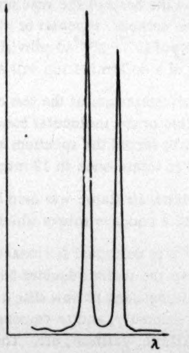


Fig. 6. Recording of the Na doublet 589.0-589.6 mμ on the spectrophotometer (slit width 0.025 mm).

The operating wavelength range indicated above is not quite suitable for flame photometry, since the analytical lines of a number of elements which it is desired to determine lie outside this range (lithium, potassium, rubidium, cesium). In order to extend the operating range of the apparatus, one of the spectrograph prisms (the small one) which is located near the output of the apparatus, was turned through a small angle, while another prism (also a small one) located near the input, was shifted through a certain angle in order to correct for the curvature of the line projected on the output slit of the apparatus. The angles through which the prisms were rotated were controlled so that the cesium line at 894.4 mμ fell within the operating range on the long wave side of the spectrum, while the magnesium band at

383 mμ fell within the operating range on the short wave side. Since the apparatus was rearranged in this way, additional focussing was necessary (on the basis of the maximum deviation of the potentiometer) on switching from the long wave side of the spectrum to the short wave side. There was no need for this focusing when determining high contents of the elements (i.e., when the value of the background was insignificant compared to the line intensity being measured), or on switching from photometric measurements of the parts of the spectrum in the cesium region (λ = 852 mμ) to the lithium region (λ =670 mμ) or from the thallium region (λ = 535 mμ) to the calcium region (λ = 422 mμ).

The FEU-18 (visible) and FEU-22 (red and infrared) photomultipliers were used for recording the light flow. Because the voltage supplied to the photomultiplier in the FEP-1 was not high enough (about 1000 v), and because of the large dark currents of the FEU-22 photomultiplier (difficult to compensate by the circuit), and the appreciable characteristic "dark" current of the amplifier of the setup, it proved inconvenient to use the amplifier and rectifier supplied with the apparatus. Instead of these, for supplying the apparatus, we used a VS-9 rectifier and a cathode repeater, the circuit of which did not differ much from that used by Poluektov and Nikonova [4]. In the setup which we used, the input resistances were increased, and the resistances of the circuit used for compensating the dark current decreased in accordance with the lower value of the dark current of the actual photomultipliers used in our work. Standard connecting elements were used for linking up the various units of the apparatus; these elements made it possible to assemble the apparatus rapidly from the requisite parts, and enabled the photomultiplier anode to be switched to the amplifier or to the cathode repeater. When necessary, measurements could also be made on the basis of the readings on the galvanometer, for which purpose the latter was connected with the output of the cathode repeater or was connected into the photomultiplier in the usual way. Measuring apparatus with a sensitivity of $10^{-7}-10^{-8}$amp/division or even a microammeter could be used in the cathode repeater circuit. The sensitivity of a determination will also be dependent on the characteristics of the measuring apparatus used.

TABLE

Element	Line or band, mμ	Sensitivity, μg/ml	Element	Line or band, mμ	Sensitivity, μg/ml	Element	Line or band, mμ	Sensitivity, μg/ml
Lithium	670.8	0.0005	Magnesium	383	0.1	Barium	553.5	0.08
Sodium	589.6	0.0001	Cesium	852.9	0.003	Gallium	417.2	0.05
Potassium	769.9	0.001	Calcium	422.7	0.005	Indium	451.1	0.05
Rubidium	794.8	0.002	Strontium	460.7	0.005	Thallium	535.0	0.05

At low concentrations of the test element, or in the presence of a large background, a small section of the spectrum (the line or the molecular band, and the adjacent background) can be recorded by means of the apparatus. It is convenient to record the spectrum at two standard rotation rates of the prism of the setup. The first permits the prism drum to rotate once in 12 min, while the second gives a rotation speed three times slower.

An acetylene-air flame was used as the excitation source. The burner, which was a Meker type, had a glass sprayer and a concave mirror which increased the sensitivity of a determination 2-3 times.

The apparatus described is characterized by a high light strength and dispersion. This enabled us, for example, to resolve the sodium doublet 589.6-589.0 mμ (Fig. 6) when the inlet and outlet slits had a width of 0.025 mm, while, by using narrow slits, it was possible to increase the selectivity of the photometric determination of elements considerably, and to decrease the flame background during the determination of calcium, strontium, magnesium, thallium, gallium, etc. The overall consequence of this is an appreciable increase in the sensitivity of determination in a flame.

An idea of the increase in sensitivity can be gained by examining the results presented in the Table.

The sensitivity of the determination of all the elements indicated is one order higher than that achieved hitherto [8]. Rubidium can be determined at this sensitivity in solutions in which the amount of potassium present is 100 times that of rubidium, while cesium can be determined in solutions in which the amount of potassium is 1000 times the cesium content; these are the conditions normally met during determination of these elements in natural materials. The sensitivity values given in the table may vary from 3 to 5 times, depending on experimental conditions (slit width, the voltage supplied to the photomultiplier, the rate at which the solution is fed into the flame, etc), and, they indicate that it should be possible to determine a number of elements (e.g., cesium) without preliminary chemical concentration.

SUMMARY

With the aim of finding possible ways of increasing the sensitivity of the determination of elements in a flame, a systematic study has been made of combined sources: flame—arc and flame—spark. It has been shown that by using amplitude discriminators, or by recording the spectra on photographic plates, it is possible to attain a considerable increase in the sensitivity of the determination of these elements in these sources.

The design of a highly sensitive recording spectrophotometer for the determination of the elements in a flame is described; this spectrophotometer is assembled from the Russian equipment ISP-51 and FEP-1. Using this equipment it is possible to increase the sensitivity of the photometric determination of a number of elements by more than one order, and to determine these elements without their preliminary chemical concentration.

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POTENTIOMETRIC METHODS OF TITRATING MULTICOMPONENT MIXTURES OF ACIDS IN NONAQUEOUS SOLUTIONS

A. P. Kreshkov, L. N. Bykova, and
N. A. Kazaryan

D. I. Medeleev Moscow Chemico-Technological Institute

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Nonaqueous solvents [1-3], because of their characteristics, are valuable media at present for a large number of very important analytical determinations which cannot be carried out in aqueous solutions; the impossibility of carrying out such determinations in aqueous solutions is determined by the insolubility of many compounds in water, by small differences in pK values, by the dissociation of electrolytes in water, and, finally, by the leveling effect of water.

The same material can behave as a strong or a weak electrolyte, or as a nonelectrolyte, depending on the nature of the solvent, and behave as an acid, base, salt, or neutral compound.

The dielectric permeability [4, 5] and the chemical nature of the solvent [6] have an essential influence on the value of the electrical conductivity coefficient $\lambda/\lambda_0 = \alpha_1$, where λ is the equivalent electrical conductivity and λ_0 is the equivalent electrical conductivity at infinite dilution.

The primary state of a material in solution has been considered by many authors [7-12]. According to Izmailov [13-15], dissociation of electrolytes proceeds in several successive stages and is accompanied by the formation of solvates and by dissociation of the solvated interaction and association product of solvated ions (this is particularly true in medium characterized by a low dielectric permeability).

In the general case, the universal scheme of the dissociation process can be represented as follows, according to Izmailov

$$\begin{array}{rl} KA + (n+m)\,M \overset{I}{\rightleftarrows} KAM_n + mM \overset{II}{\rightleftarrows} & K^+_{salt} + A^-_{salt} \\ & \quad\downarrow\uparrow\ {}^{III} \\ {}^{+}yM \overset{IV}{\rightleftarrows} & K^+_{salt}A^-_{salt} + xM. \end{array}$$

The general equation, which reflects all the equilibria which are established in the medium of a given solvent, is expressed as follows:

$$K_{ord.} = \frac{K_{diss.}}{1 + K^*_{inst.} + K_{conv.}},$$

where $K_{ord.}$ is the electrolytic dissociation constant of the electrolyte as determined by the usual (ordinary) methods; $K^*_{inst.}$ is the equilibrium constant (I) expressing the formation of addition compounds between the electrolyte molecules and solvent molecules; the index [*] shows that K refers to an infinitely dilute solution; $K_{diss.}$

is the equilibrium constant (II) which expresses the dissociation of the addition product formed into ions; $K_{conv.}$ is the equilibrium constant (IV) which is the reaction constant for the conversion of the nonionized addition product into an ion pair.

The equilibrium constant (III) expresses the formation of ion pairs, $K^{-1}_{assoc.} = K^{-1}_{diss.} K^{-1}_{conv.}$ or $K_{diss.} = K^{-1}_{assoc.} K_{conv.}$

This equation can acquire various values for a number of special cases. Berg, Patterson [16], Correy [17], Sadek and Fuoss [18], and Kolthoff and Bruckenstein [19, 20] have derived analogous equations which are really special cases of the general equation.

The stronger the basic properties of a solvent, the stronger are its effect on weak acids. In basic solvents which have a high dielectric permeability and dipole moment, the strength of an acid increases. The stronger the acid properties of a solvent, the greater are its effect on weak bases. In acid solvents which have a high dielectric permeability and low autoprotolysis constants, the strength of a base increased. Thus, manifestation of acid or basic properties by the dissolved material is determined, not only by the dielectric permeability, but also by the chemical properties of the solvent.

Accordingly, the behavior of an electrolyte in a given solvent is determined not only by the properties of the electrolyte itself, but also by the properties of the solvent chosen. By choosing between solvents which possess different properties, it is possible to obtain solutions of electrolytes which behave differently. For example, the change in acid strength which occurs on switching from one solvent to another can be expressed by the following equation:

$$\Delta pK = pK_M - pK_{H_2O} = 2 \lg \gamma_0 \text{ions} - \lg \gamma_0 \text{molecule}$$

where, ΔpK is the difference between the pK values in the two solvents, e.g., in an organic solvent (M) and in water (H_2O); γ_0 are single activity coefficients relating to the state of the material in an infinitely dilute aqueous solution.

The basis of the theory of acid–base titration in nonaqueous solution has been developed by Izmailov [15].

The accuracy of a titration is determined by the ratio of the autoprotolysis constant (ionic product) of the medium K_i^* to the usual dissociation constant $K_{ord.}$ of the acid or base, $K_i^* / K_{ord.}$

The accuracy of a differential titration of acids or bases is determined by the ratio of their strength: $K_{ord.II}/K_{ord.I} = K_T$, where K_T is a titration constant which remains constant in an aqueous medium, but changes strongly with the solvent.

The smaller the value of K_T, the lower is the titration error. The limiting value of K_T should not exceed 10^{-4}. By choosing appropriate nonaqueous solvents it is possible to alter the ratios

$$\frac{K_i^*}{K_{ord}} \text{ and } \frac{K_{ord\,II}}{K_{ord\,I}},$$

considerably, so that it is possible to titrate materials in nonaqueous media which cannot be titrated in aqueous solutions.

The theory of the erros involved in the separate titration of mixtures of acids and bases has been developed by Roller [21]. Thus, the results and accuracy of acid–base titration depend not only on the titrimetric determination chosen, the titrant used, the concentration of the reactants, and the temperature of the solution being titrated, but also to a large extent on the character and nature of the solvent, which have a decisive influence on the strength of the acids and bases determined.

The work described here, which was based on the theoretical principles outlined above, was carried out with the object of developing methods for the differential titration of multicomponent acid mixtures.

EXPERIMENTAL

The acid mixtures were titrated by indicator, potentiometric, conductometric, and high frequency methods.

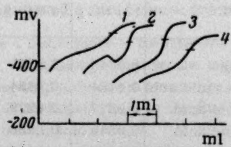

Fig. 1. Potentiometric titration curves for compounds which possess acid properties and cannot be titrated in water. 1) o-Cresol; 2) resorcinol; 3) α-naphthol; 4) pyrocathechol.

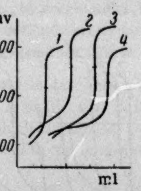

Fig. 2. Potentiometric titration curves for water insoluble acids. 1) Caproic acid; 2) caprylic acid; 3) pelargonic acid; capric acid.

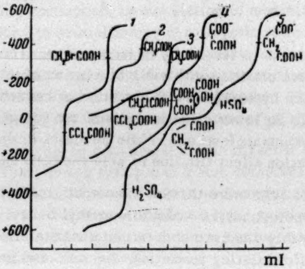

Fig. 3. Potentiometric titration curves for two component acid mixtures; 1) Trichloroacetic and bromoacetic acids; 2) trichloroacetic and acetic acids; 3) monochloroacetic and acetic acids; 4) salicylic and oxalic acids; 5) sulfuric and malonic acids.

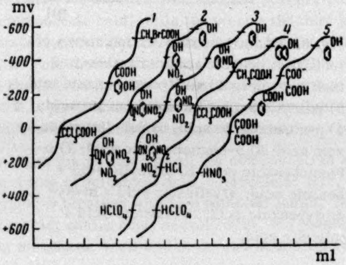

Fig. 4. Potentiometric titration curves for multicomponent acid mixtures. 1) Trichloroacetic + salicylic + bromoacetic acids; 2) picric acid + 2,6-dinitrophenol + p-nitrophenol; 3) picric acid + 2,4-dinitrophenol + o-nitrophenol + phenol; 4) perchloric acid + hydrochloric acid + trichloroacetic acid + acetic acid + β-naphthol; 5) perchloric acid + nitric acid + oxalic acid + benzoic acid + phenol.

As our work showed, the indicator method of titrating mixtures of acids has only limited application, since the presence of two or three (and sometimes a larger number) components in a mixture does not allow the possibility of choosing indicators, the color change ranges of which would correspond to the several equivalent points. Moreover, in strongly colored and oxidizing media, indicators cannot in general be used.

The potentiometric method permits determination of a large number of the components of mixtures in nonaqueous solutions. The high frequency is no direct contact between the solution and the electrodes; this is of particular importance for the titration of nonaqueous solutions. The fact that there is no direct contact means that it is possible to exclude the effects of polarization, adsorption, and oxidation–reduction reactions on the surface of the electrodes—effects which often distort the results of conductometric titration. Taking into account what has been said above, we decided to concentrate on two methods: potentiometric and high frequency. The work described here is devoted to the potentiometric determination of mixtures of acids. The titrant we used was tetraethylammonium hydroxide, which, as indicated earlier [22] has considerable advantages over other basic titrants. It dissolves readily in organic solvents and forms readily soluble salts with acids, while the glass electrode

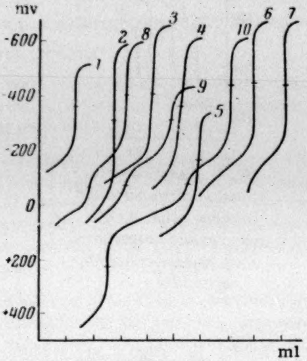

Fig. 5. Potentiometric titration curves of individual benzoic acid derivatives and their mixtures. 1) m-Hydroxybenzoic acid; 2) salicylic acid; 3) o-nitrobenzoic acid; 4) p-nitrobenzoic acid; 5) 2,5-dinitrobenzoic acid; 6) o-bromobenzoic acid; 7) p-bromobenzoic acid; 8) salicylic acid + benzoic acid; 9) salicylic acid + m-hydroxybenzoic acid; 10) sulfuric acid + salicylic acid.

Determination of Some Benzoic Acid Derivatives

Acids determined	Taken, g	Found, g	Error(relative),%
Salicylic acid	0.0343	0.0341	−0.6
m-Hydroxybenzoic acid	0.0484	0.0484	0.0
o-Nitrobenzoic acid	0.0227	0.0229	+0.9
p-Nitrobenzoic acid	0.0546	0.0550	+0.7
o-Bromobenzoic acid	0.0297	0.0295	−0.6
p-Bromobenzoic acid	0.0338	0.0341	+0.9
3,5-Dinitrobenzoic acid	0.0461	0.0464	+0.6
Salicylic +	0.0381	0.0383	+0.5
benzoic acid	0.0557	0.0555	−0.4
Salicylic +	0.0465	0.0469	+0.8
m-hydroxybenzoic acid	0.0623	0.0620	−0.5
Salicylic +	0.0412	0.0416	+0.9
sulfuric acid	0.0134	0.0135	+0.7

does not loose its sensitivity in its presence. The best results were obtained with a 0.1 M solution of tetraethylammonium hydroxide in a 5:1 mixture of benzene and methanol. At lower concentrations of the titrant the equivalence points are less sharp, while increases in the titrant concentration affect titration of acid mixtures unfavorably.

The acids were titrated in acetone, methyl ethyl ketone, methyl butyl ketone, and methyl benzyl ketone, which readily dissolved both the original materials and the materials formed during titration; in addition, they possess differentiating properties. Acetone and methyl ethyl ketone possess approximately equal differentiating properties, but the acid salts formed during titration are more soluble in methyl ethyl ketone. Methyl butyl ketone and methyl benzyl ketone were given less attention, since the first of these solvents usually contains a large number of detrimental impurities which have to be removed, while the second is too expensive.

The experimental technique and the preparation of the titrant have been described in [22].

The following compounds were titrated: phenol, acetic and benzoic acids and their derivatives, and also their mixtures with organic and inorganic acids.

Results for the titration of individual acids and their mixtures are given in Figs. 1-5. In Fig. 1 are shown the titration curves of compounds which cannot be titrated in water because of their low dissociation constants. Derivatives of phenol and naphthol possess very weak acid properties, so that it is impossible to establish the titration end point in aqueous media. In a methyl ethyl ketone medium the acid properties of these compounds increase, and such compounds as o-cresol, resorcinol, pyrocatechol, and α-naphthol can be titrated in nonaqueous media. Titration curves for the following acids which are insoluble in water are shown in Fig. 2: caproic, caprylic, pelargonic, and capric acids. In methyl ethyl ketone these compounds behave as relatively strong acids and so can be titrated in nonaqueous media.

A comparison of the titration curves of individual acids with the titration curves of their mixtures shows that in a methyl ethyl ketone medium, differential titration is possible in those cases where the beginning of the potential jumps of the individual acids differ by more than 100 mv. Thus, in the case of the titration curves of acetic acid and its chlorinated derivatives, the difference between the beginning of the potential jumps of acetic and trichloroacetic acids is 400 mv, while the difference between the potential jumps for acetic and monochloroacetic acids is 100 mv. Titration curves for acetic acid plus trichloroacetic and monochloroacetic acids are shown in Fig. 3 (Curves 2, 3).

Two clearly defined potential jumps are observed on the titration curve for a mixture of trichloroacetic and acetic acids; on the titration curve for a mixture of monochloroacetic and acetic acids, however, the potential jump corresponding to neutralization of monochloroacetic acid is not defined clearly enough. Trichloroacetic acid is a stronger acid than bromoacetic acid and can be determined in its presence (Curve 1).

Curve 4 corresponds to the titration of a mixture of a dibasic acid (oxalic acid) and a monobasic acid (salicylic acid). In a methyl ethyl ketone medium, salicylic acid is as strong as oxalic acid in its first dissociation stage. Accordingly, there are two jumps one the titration curve, one of which corresponds to neutralization of salicylic acid and oxalic acid to the first stage, while the second corresponds to the second stage in the neutralization of oxalic acid.

Two potential jumps are observed during the titration of sulfuric acid in a methyl ethyl ketone medium. This fact permits the determination of sulfuric acid in its mixtures with mono- and dibasic acids. Thus, during the titration of a mixture of sulfuric and malonic acids (Curve 5) four potential jumps are observed: the first corresponds to the first stage in the neutralization of sulfuric acid, the second to the first stage in the neutralization of malonic acid, the third to the secondstage in the neutralization of sulfuric acid, and the fourth to the second stage in the neutralization of malonic acid.

Titration curves of multicomponent mixtures are shown in Fig. 4. During the titration of mixtures of the three acids: trichloroacetic, salicylic, and bromoacetic acids,Curve 1 with three potential jumps is obtained. The first jump corresponds to completion of neutralization of trichloroacetic acid, while the second and third jumps correspond to neutralization of salicyclic and bromoacetic acids respectively. In methyl ethyl ketone, salicyclic acid is a stronger acid than bromoacetic acid, whereas in water both these acids have the same pK value of 3. Curves 2 and 3 were obtained during titration of mixtures of phenol and its nitro derivatives. Nitro groups enhance the acidity of the phenolic hydroxyl. This means that it is possible to obtain a titration curve with four jumps during the titration of a mixture of picric acid, dinitrophenol, mononitrophenol, and phenol.

Titration in nonaqueous media makes it possible to establish the presence of all the components in a mixture. Thus, during titration of a five component mixture consisting of perchloric acid, hydrochloric acid, trichloroacetic acid, acetic acid, and β-naphthol, a titration curve is obtained with five potential jumps. During titration of a mixture of the five acids, perchloric acid, nitric acid, oxalic acid, benzoic acid, and phenol, a curve is obtained with six potential jumps corresponding to the four monobasic acids and to the two neutralization steps of the dibasic oxalic acid.

Accordingly, titration of a mixture of acids in a differentiating solvent medium enables one to obtain curves with several potential jumps, so that it is possible to analyze multicomponent mixtures of acids.

The table contains results for the quantitative determination of individual benzoic acid derivatives and their mixtures. The titration curves of these compounds are shown in Fig. 5.

Several aliquots of each sample were analyzed. The determination was regarded as satisfactory when not less than three results coincided. As is evident from the table, individual acids and their mixtures can be determined with an accuracy of some tenths of a percent.

SUMMARY

A study has been made of the titration of derivatives of phenol, acetic and benzoic acids, as well as of mixtures of these compounds with organic and inorganic acids; the titrant was tetraethylammonium hydroxide in various organic solvents. It has been established that in a methyl ethyl ketone medium it is possible to titrate multicomponent mixtures consisting of three, four, and even five acids. The accuracy with which the acids mentioned can be titrated individually, or in their mixtures, is some tenths of a percent.

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THE EFFECT OF OXYGEN ADSORPTION ON THE OXIDATION OF FERROCYANIDE IONS ON A GOLD ELECTRODE

O. L. Kabanova

V. I. Vernadskii Institute of Geochemistry
and Analytical Chemistry, Academy of Sciences,
USSR, Moscow

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The development of electroanalytical methods (coulometric titration, potentiometric and amperometric titrations during the passage of a current, etc.) requires a study of electrode reaction mechanisms under various conditions. The mechanism of an electrode reaction often depends on changes in the surface properties of the electrode used, on switching over from the pure metal to metal which has adsorbed hydrogen, oxygen, or various ions from solution. Adsorption is of particular importance for solid electrodes (platinum, gold, etc.) which are used in the region of positive potentials within which mercury dissolves, and are used for the analytical determination of systems with electrochemical properties similar to those of the system Hg, Hg^{n+}.

The platinum electrode is the most commonly used electrode in analytical chemistry; the gold electrode, however, has a number of advantages over the platinum electrode, the main advantage being its considerably wider useful potential range; for gold this is approximately 0.0-1.0 v relative to the normal hydrogen electrode (N.H.E.) in $HClO_4$ [1] from which oxygen has been removed, while for platinum this range is limited to 0.4-0.8 v [2]. The main reason for this difference is that on a gold electrode, the amount of hydrogen adsorbed is extremely low, while the adsorption potential for oxygen is high, as compared with a platinum electrode. It has been shown in the case of a platinum electrode [3] that adsorption of oxygen on the electrode leads to an essential change in the rate of the oxidation–reduction reactions, and, accordingly, leads to distortion of the polarization curves. The characteristics of the mechanisms of oxidation–reduction reactions have been studied to a considerably lesser extent on gold than on platinum electrodes.

In this connection therefore we thought that it would be expedient to study the effect of oxygen adsorption on a gold electrode during the course of some typical oxidation–reduction reaction which is of analytical interest. A suitable system for this purpose is the ferrocyanide–ferricyanide system.

It is known from published data that oxidation of ferrocyanide ions on a gold electrode [4-6] may be accompanied by polarization to varying extents. It has also been pointed out that the reaction rate drops when the gold is oxidized [7].

The work described here was devoted to a quantitative study of the rate of oxidation of ferrocyanide ions on a gold electrode as a function of the degree of passivity of the electrode in perchloric acid solutions.

The electrochemical properties of a gold electrode in pure perchloric acid solutions should be similar to those of the electrode in sulfuric acid solutions. The following published information is available on such properties in sulfuric acid solutions. During anodic polarization, it has been observed in a number of papers [8-11] that there is only one potential delay at 1.3-1.4 v, which is explained by the formation of a unimolecular film of Au_2O_3, and one cathodic delay at 1.0-1.1 v corresponding to the reduction of surface oxide. Spectrographically pure gold whose surface is originally pure, and less pure gold containing 0.05% of impurities, behave similarly with respect to their electrochemical properties [11]. Will and Knorr [2], during a study of the passivity of a smooth gold electrode, used a method which they have suggested [12] of taking rapid anodic and cathodic polarization curves without turning off the current. On taking polarization curves for gold in 8 N H_2SO_4, the rate at which the potential changed being 1 v/sec, they found that adsorption of oxygen starts at 1.37 v, oxygen being removed up to 0.85 v; the maximum amount of oxygen is removed at 1.1 v. In other papers [13, 14] other delays have been observed on the anodic curve; these can be ascribed to the presence of impurities in the metal [11]. Thus, the potential delay observed [15] at 0.76-0.85 v is related [11] to the presence of accidental contamination by iron. Nevertheless, it can be assumed that oxidation of gold on its surface does not only occur at potentials of 1.3-1.4 v. In fact, the amount of electricity consumed during anodic polarization of gold up to 1.2 v is approximately 50 μ coul/cm^2 per 0.1 v [11], which is considerably in excess of the amount of electricity necessary for changing the double layer (10 μ coul/cm^2 per 0.1 v for the positively charged surface of the solid electrode). The excess electricity is, obviously, used up on the adsorption of the fraction of the oxygen in the monolayer at potentials below 1.2-1.3 v, while at more positive potentials, monolayers and polylayers of oxygen are formed on the gold [9, 15].

Baumann and Shain [1] have taken polarization curves on a rotating gold electrode in the form of a wire, using perchloric acid of varying concentrations; the rate at which the potential was applied was varied while the electrode was subjected to different treatments. On the basis of their results [1], in 1 N $HClO_4$, and when the rate of change of potential is 3.7 mv/sec, oxidation of gold starts at 1.3-1.4 v relative to the normal hydrogen electrode; only the main part of the oxygen is removed at 1.1 v, the remainder being removed at less positive potentials.

From an analysis of the work outlined above, it can be concluded that adsorption and desorption of oxygen on gold, as a rule, occur with appreciable overvoltage; the oxygen is removed at potentials which are 0.2-0.3 v less positive than those at which it is adsorbed. Up to 1.3 v relative to the normal hydrogen electrode, oxygen is adsorbed in amounts which are considerably less than those found in the monolayer, while it is removed below 1.1 v.

Method. The oxidation kinetics of ferrocyanide ions were studied in 1 N and 10^{-3}N $HClO_4$. The acid was twice distilled. The $K_4Fe(CN)_6 \cdot 3H_2O$ was recrystallized twice from twice-distilled water.

The work was carried out on a smooth gold disc electrode with a surface area of 0.058 cm^2; it was rotated at a speed of 3000 rpm. A platinized platinum electrode immersed in the same solution served as the second electrode. Polarographic curves were taken with a Heyrovsky polarograph. During the time the curves were being taken, the potential of the gold electrode was measured by a compensation method relative to the hydrogen electrode in a perchloric acid solution of the appropriate concentration. The experiments were made at a temperature of 25 ± 0.1 °C. in an atmosphere of purified nitrogen [3].

Prior to taking the curves, the gold electrode was usually kept at a potential of $\varphi = 1.5$ v, and then at $\varphi = 0.5$ v relative to the normal hydrogen electrode. The curves were taken from 0.2 v to the chosen value (1.0-1.9 v) and then back again. In some of the experiments the apparatus was momentarily switched from forward into reverse, while in some of these experiments the electrode was kept at the chosen potential value for 15 min and the reverse curve then taken. The rate of potential change was 400 mv/min.

EXPERIMENTAL

Typical polarographic curves for the oxidation of ferrocyanide ions on a gold electrode in 1 N $HClO_4$ are shown in Fig. 1. The ferrocyanide ion concentration was $3\text{-}4 \cdot 10^{-4}$M. Curve 1 in Fig. 1 was taken from 0.2 to 1.9 v, and the reverse curve 1' taken immediately. Curve 2' is the reverse curve obtained after the potential had been kept stable at 1.90 v for 15 min, while curve 3' is the reverse curve for the oxidation of ferrocyanide ions after the potential had been kept constant at 1.60 v. Curve 4 was taken in pure 1 N $HClO_4$, while curve 4' is the corresponding reverse curve obtained after keeping the potential stable in 1 N $HClO_4$ at 1.9 v.

Similar oxidation curves for the ferrocyanide ions were obtained in 10^{-3}N $HClO_4$.

The polarograms taken in the pure acid were found to be independent of the changes in the rate at which the electrode was rotated, in both 10^{-3}N and in 1 N $HClO_4$.

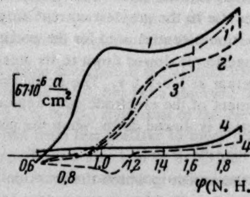

Fig. 1. Polarograms for the oxidation of ferrocyanide ions on a smooth gold electrode in 1 N $HClO_4$. Curve 1 was taken from less positive to more positive values. Curve 1' is the corresponding reverse curve. Curve 2' and 3' are the reverse curves obtained after keeping the potential stable at 1.90 v (Curve 2') and 1.60 v (Curve 3'). Curves 4 and 4' are the forward and reverse curves for 1 N $HClO_4$, in which the potential was stablized at 1.90 v.

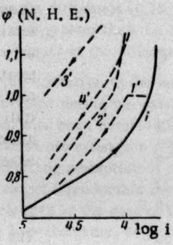

Fig. 2. Polarization curves for the oxidation of ferrocyanide ions on an unoxidized gold electrode (Curve 1) and on oxidized gold electrodes (Curves 1', 2', 3', and 4'). The reverse curves (dotted lines) were taken after the electrode potential had been kept constant at 1.00 v (Curve 1'), 1.30 v (Curve 2'), 1.60 v (Curve 3'), and 1.90 v (Curve 4').

In Fig. 2, the experimental results obtained on the oxidation of ferrocyanide ions in 1 N $HClO_4$ are expressed as a relation between the logarithm of the current density (log i) and electrode potential (φ). The curves are given after deduction of the current value in pure perchloric acid. The reverse curves (1', 2', 3', and 4') given in Fig. 2 were taken after the potential had been kept constant (stabilized) for 15 min at 1.00, 1.30, 1.60, and 1.90 respectively. From the curves shown in Figs. 1 and 2 it is quite clear that the oxidation current is appreciably less when the reverse curves are taken. The slope of the reverse curves in the current density range considerably lower than the limiting range, is 2-3 times greater. Similar curves were obtained in 10^{-3}N $HClO_4$, and also on instantaneous switching from the forward to reverse directions; in the latter case, however, the current drop becomes appreciable when the switching is carried out at 1.30 v, but not at 1.00 v.

On the ordinate in Fig. 3 is shown the observed decrease in the oxidation current of ferrocyanide ions (Δlog i = log i − log i', where i is the current density in the forward direction, and i' is the current density in the reverse direction) as a function of the potential of the polarized electrode when the potential was kept constant at different values for 15 min in 1 N $HClO_4$. It is clear from these results that the slowing down of the reaction increases on increasing the intermediate polarization potential (the value at which the potential is kept constant) from 1.00 to 1.60 v, at which it has slowed down by an order of one and a half; keeping the potential constant at 1.90 v again leads to an increase in the reaction rate; it does not, however, reach the rate of oxidation of ferrocyanide ions in the forward direction. The reaction is slowed down to its maximum extent at 0.90 v, the slowing down then decreases as the region of the limiting diffusion current is reached, within which the rate is not determined by overvoltage.

Similar curves for the oxidation of ferrocyanide ions were obtained in 10^{-3}N $HClO_4$. For the curves shown in Fig. 4, preliminary activation of the electrode was carried out at 0.52 and 1.52 v relative to the normal hydorgen electrode. Similar results were also obtained when preliminary activation of the electrode was carried out at 0.32 and 1.32 v relative to the normal hydrogen electrode. Maximum slowing down of the reaction was observed in both cases at 0.6 v. When the decrease in current observed at this potential is expressed as a function of the values at which the potential was kept constant, Curve 1, Fig. 5, is obtained, corresponding to the results in Fig. 4. Curve 2, Fig. 5, was obtained from the experiments in which activation was carried out at 0.32 and

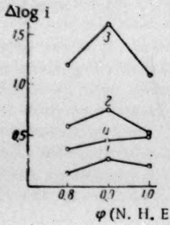

Fig. 3. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the electrode potential in 1 N $HClO_4$; the potential is kept constant at the following values: 1.00 v (Curve 1); 1.30 v (Curve 2); 1.60 v (Curve 3); 1.90 v (Curve 4).

1.32 v. A comparison of curves 1 and 2, Fig. 5, shows that the decrease in current, and the value of the constant potential (the value at which the potential is kept constant) which gives rise to the greatest current drop, depend only to a small extent on the activation potential used for the preliminary treatment of the electrode. The reaction is slowed down to its greatest extent when the potential is kept constant at 1.0-1.3 v. The activation potentials used for the preliminary treatment of the electrode only appreciably affect the extent to which the reaction is slowed down when the potential is kept constant at values higher than 1.30 v.

Curve 3, Fig. 5, which shows the extent to which the reaction is slowed at 0.9 v, is a similar curve for the oxidation of ferrocyanide ions in 1 N $HClO_4$. The maximum decrease in the current is observed when the potential is kept constant at 1.60 v. The current drop in 1 N $HClO_4$ is half of an order higher than in 10^{-3}N $HClO_4$.

In our opinion the drop in the oxidation current of ferrocyanide ions is explained by adsorptive passivation of the gold electrode. Adsorption of oxygen, which leads to the greatest slowing down effect, occurs in the potential range above 1.00 v relative to the normal hydrogen electrode, while removal of the adsorbed oxygen occurs at potentials which are appreciably less positive; i.e., adsorption and desorption occur with overvoltage, which leads to hysteresis on the oxidation curves for gold taken in the forward and reverse directions. A similar hysteresis effect has been observed during the oxidation of divalent iron on gold and platinum [1, 3]. Slowing down increases as the amount of adsorbed oxygen accumulates or during the aging of the adsorbed layer (an effect caused by keeping the potential constant for some time). What was unexpected was that the slowing down only increases up to a certain value of the stabilized potential (the value at which the potential is kept constant); when the latter is increased further, the slowing down decreases. This phenomenon has not been observed during the oxidation of iron on a platinum electrode [3], although the slowing down has been observed to decrease even in this case on increasing the adsorption potential of oxygen on the platinum from 1.2 to 1.4 v. Such a form of the relationship between the slowing down and the value of the stabilized potential may be explained on the assumption that it is the adsorbed oxygen which exhibits this slowing down effect, while the layer of phase oxide does not exhibit an appreciable slowing down effect.

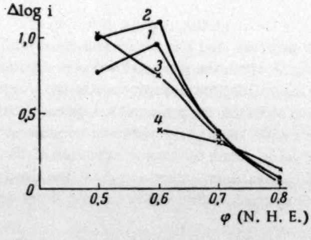

Fig. 4. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the electrode potential in 10^{-3}N $HClO_4$, when the potentials were kept constant at the following values: 1.02 v (Curve 1); 1.32 v (Curve 2); 1.62 v (Curve 3); and 1.92 v (Curve 4).

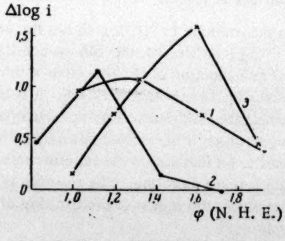

Fig. 5. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the values at which the electrode potential is kept constant, for the following potentials of the polarographic curve: 0.60 v (Curves 1 and 2, 10^{-3}N $HClO_4$); and 0.90 v (Curve 3, 1 N $HClO_4$).

The difference between the stabilized potentials which give the maximum current drop in 1 N $HClO_4$ and in 10^{-3}N $HClO_4$, and which is equal to 0.30-0.50 v, has the same sign as the difference (0.18 v) in the adsorption potentials of oxygen on gold at pH values of 3 and 0 [10]; nevertheless, it is greater than the latter. This, presumably, can be explained by differences in the structure of the adsorbed layer at the different pH values.

A sharp decrease in the current strength at a potential of about 1.50 v relative to the normal hydrogen electrode (see [16]), has been observed in some cases on a platinum electrode during the oxidation of ferrocyanide ions in 0.1 N H_2SO_4; hysteresis of the curves similar to that described has also been observed when these curves were taken from less positive to more positive potentials, and in the reverse direction (see [3]). The results of these experiments also can be explained by passivation of the electrode during adsorption of oxygen on it, and removal of oxygen occurring with overvoltage. Nevertheless, in order to get reproducible results with a platinum anode it is necessary to be much more strict in observing the conditions than in the case of a gold electrode; the conditions used for preliminary activation of the electrode must be kept the same, as well as the initial and final potentials of the oxidation curve. This fact is one reason in favor of the use of a gold electrode as an anode in analytical chemistry.

Nevertheless, even when a gold electrode is used in the potential region within which gold is oxidized, it is necessary to take into account the influence of the passivizing action of oxygen on the course of the oxidation—reduction reactions.

It follows from our results that the potential range within which the gold electrode can be used for automatic polarographic determination of ions can be extended in some cases to 1.5-1.6 v in the positive direction. Under these conditions, it is essential to use either curves taken from less positive potentials to more positive potentials, or to use the reverse curves when the electrode reaction is only slowed down to a relatively small extent by the adsorption of oxygen on the gold electrode.

In cases of intermittent changes in the current or potential of the gold electrode within the potential range where adsorption of oxygen occurs, it is necessary to activate the electrode before measuring each point, by switching anodic and cathodic polarizations, and to take a reading after definite time intervals from the start of electrolysis.

I should like to thank A. N. Frumkin and B. N. Kabanov for taking part in the discussion of results.

SUMMARY

Anodic oxidation of ferrocyanide ions in 1 N and 10^{-3}N $HClO_4$ has been studied polarographically on a rotating gold electrode.

Adsorption of oxygen on gold decreases the rate of oxidation of ferrocyanide ions by an order of 1-1.5.

The reaction of the ferrocyanide ion is slowed down to a greater extent in 1 N $HClO_4$ than in 10^{-3}N $HClO_4$.

Slowing down of the oxidation of ferrocyanide ions increases on increasing the potential at which oxygen is adsorbed to a definite value of 1.60 v in 1 N $HClO_4$ and 1.1-1.3 v in 10^{-3}N $HClO_4$; the slowing down thereafter decreases.

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A STUDY OF THORON AND ITS REACTIONS WITH SEXIVALENT URANIUM

V. A. Mikhailov

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Organic reagents containing the o-arsono-o-hydroxyazo group have been recommended by Kuznetsov [1-3], and are finding ever increasing use in analysis. Thus, thoron has been used for the determination of thorium [4-9], zirconium [10], quadrivalent uranium [11], quadrivalent plutonium [12], beryllium [13], and lithium [14]; arsenazo has been used for the determination of sexivalent uranium [15], the rate earths [16], zirconium [17], aluminum [18], and other elements. Of considerable interest in this connection is the study of the properties of these reagents and of the compounds which they form, establishment of the effect of pH, and clarification of the reaction mechanism. Work along these lines has appeared in recent years, and thoron [19-21], arsenazo [22], and their compounds [6, 11-14, 21, 23, 24] have been examined. One drawback of some of these papers is that the pH of the media have only been examined over comparatively narrow ranges. As a consequence the experimental results are not treated accurately.

1. The Behavior of Thoron at Various pH Values

Thoron has been examined spectrophotomerically earlier by Adamovich and Didenko at pH 1.4-12.6 [19], Margenum at pH 5-13.5 [20], and Byrd [21]. In the work described here spectrophotometric studies were carried out within the pH range -1 to 15. They were supplemented by electrophoretic results.

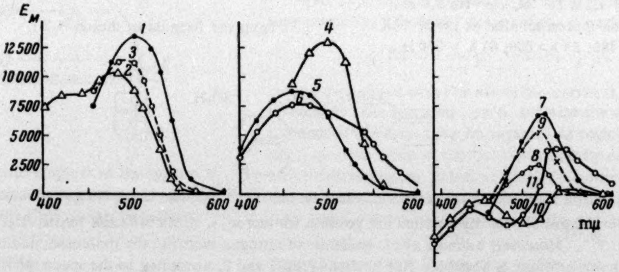


Fig. 1. Absorption curves for thoron at various pH values. Reference solution, water. 1) pH 1; 2) pH 0-3; 3) pH 5-7; 4) pH 9-10; 5) pH 12-13; 6) pH 15. Reference solution, thoron solution at pH 1; 7) pH 1; 8) pH 5-7; 9) pH 9-10; 10) pH 12;13; 11) pH 15.

A 0.2% aqueous solution of commercial thoron was prepared; the commercial material contains 78% of 1-(2-arsonobenzolazo)-2-hydroxynaphthalene-3,6-disulfonic acid. The amount of the principal component of the material was determined in two ways: 1) by drying at 150°, and calcining at 1100°, the amount of water and nonvolatile impurities were determined; 2) by spectrophotometric titration of thoron with a thorium salt in 0.1 M acid; thoron and thorium interact in the ratio of 2 :1 [4]. The optical density was measured on a SF-4 spectrophotometer using glass cuvettes with layer thicknesses of 1.0 and 2.0 cm. The thoron concentration was 1.2×10^{-4} M.

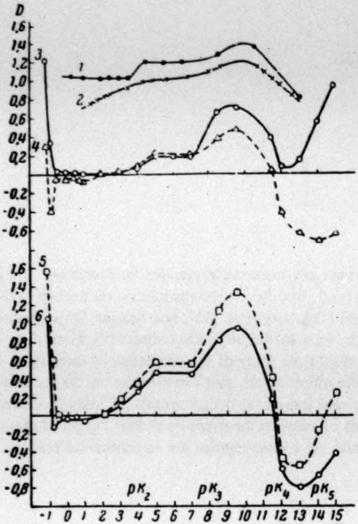
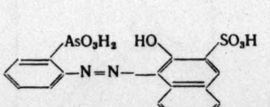


Fig. 2. Effect of pH on the light absorption of thoron solutions. 1) Thoron 1.2×10^{-4}M, cuvette 1.0 cm, λ = 500 mμ, reference solution-water; 2) Adamovich and Didenko's results [19], λ =490 mμ; 3-6) thoron 1.2×10^{-4}M, cuvette 2.0 cm, reference solution-thoron solution at pH 1; 3) λ = 540 mμ; 4) λ = 480; 5) λ = 520; 6) λ = 500 m μ.

The color of thoron solutions depends on the pH; in concentrated hydrochloric acid the color is raspberry, while in dilute acid it is orange, and in a weakly alkaline (ammoniacal buffer solution) medium it is reddish; in dilute alkaline solutions it is yellow, and in concentrated alkaline solutions raspberry. These color changes of the solutions are reversible. The absorption curves of thoron solutions at some of the most characteristic pH values: -1, 0-2, 5-7, 9-10, 12-13, and 15 are given in Fig. 1. The optical density was measured with respect to a solution of thoron at pH 1, and also with respect to water. The latter curves were obtained from the former by adding the absorption of the reference solution to them.

As is evident from Fig. 2, which expresses the relationship between the light absorption of thoron solutions at various wavelengths and pH, the curves in Fig. 1 belong to various states of thoron. A characteristic feature of these states is the horizontal sections at the extremes or ends of the curves in Fig. 2. It can be assumed, as other authors have done [19-22], that these states are various stages in the dissociation of thoron. The maximum values of the light absorption and the molar coefficients for the various forms of thoron are given in Table 1.

From the formula of thoron H_5T:



it is clear that five stages of acid dissociation are possible for thoron, i. e. six different forms: H_5T, H_4T^-, H_3T^{2-}, H_2T^{3-}, HT^{4-} and T^{5-}. Moreover, because of the presence of nitrogen atoms in the molecule, addition of H^+ ions to give a seventh (onium)form is possible: H_6T^+. From Figs. 1 and 2, according to the spectrophotometric results at various pH's, only six different forms of thoron can be distinguished, while only five at the best can be distinguished visually.

In order to avoid possible arbitrariness in interpreting the curves in Fig. 2, electrochromatographic experiments were carried out on the transport of the various forms of thoron [25]. A few drops of thoron solution at a given pH was placed on the middle of a sheet of filter paper 30 cm long and 1-2 cm wide. The remainder of

TABLE 1

Maximum Light Absorption of Thoron at Different pH Values

pH	Reference solution–water		EE_{490}, according to [19]	Reference solution – thoron at pH 1		
	λ_{max} mμ	$E_{\lambda max}$		λ_{max} mμ	$E_{\lambda max}$	E_{540}
—1	510	14 000	—	530	7000	5000
0—3	480	11 000	7300	—	—	—
5—7	490	13 000	9800	520	2500	600
9—10	490	14 000	11 400	520	5000	3000
12—13	460	9 000	—	560	450	250
15	470	8 000	—	540	4000	4000

TABLE 2

Electrochromatographic Behavior of Thoron

Medium	Movement of thoron	
	direction	rate cm/min 10^5
pH-1(11 M HCl)	Toward the cathode	-50 ± 10
pH-0.8(6 M HCl)	Toward the anode	+50 ± 10
pH 1(0.1 M HCl)	" "	+25 ± 15
pH 5(acetate buffer solution)	" "	+17 ± 3

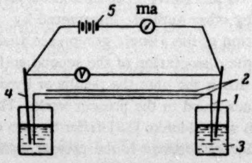


Fig. 3. Schematic diagram of the apparatus used for electrochromatography. 1) Sheet of filter paper; 2) glass plates; 3) beakers containing the solutions; 4) carbon electrodes; 5) dc source.

the sheet was moistened with a solution of the same pH. The paper was placed between two glass plates, while the ends of the paper were placed in beakers containing buffer solutions. Carbon electrodes were immersed in these beakers and a dc current at a voltage of 100-400 v (Fig. 3) passed through them for 0.5-1 hr.

From the results obtained (Table 2) it is clear that in a medium with a pH of -1, thoron is positively charged, while in media with pH higher than -0.8 it is negatively charged. Accordingly, in concentrated hydrochloric acid the form H_6T^+ is present, while at pH 0 to 3 presumably H_4T^- is present. Next, it is obvious that at pH 5-7 H_3T^{2-} predominates, while at pH 9-10, H_2T^{3-} is the main component, at pH 12-13, HT^{4-}, and at pH 15, T^{5-}. These observations, therefore, do not confirm the assumptions made by other authors [19-21] that the predominating thoron form at pH 1-2 is H_3T^{2-}. In each case the treatment adopted by other authors agrees to a lesser extent with the curves in Fig. 2 than the results given here.

An approximate evaluation of the successive dissociation constants of thoron by means of the equation:

$$H_nT^{(5-n)--} \rightleftarrows H_{n-1}T^{(6-n)-} + H^+$$

can be carried out with the aid of the curves in Fig. 2. As noted above the horizontal parts, and also the extremes and the ends of the curves, can be regarded as regions in which the respective forms of thoron predominantly exist. In the intermediate regions, points at which 50% dissociation occurs can be found. At these points the light absorption has an intermediate value between the extreme values, and the concentrations of $H_nT^{(5-n)-}$ and $H_{n-1}T^{(6-n)-}$ are equal. From the expression for the dissociation constant:

$$K = \frac{[H_{n-s}T^{(6-n)-} \quad H^+]}{[H_nT^{(5-n)-}]}$$

it is clear that K is numerically equal to $[H^+]$, and $pK = (pH)_{50\%}$. These pK values are given in Fig. 2 and in

TABLE 3

Indices of the Dissociation Constants of Thoron

Dissociation scheme	The groups in thoron which participate in the reaction	According to Fig. 2	According to published results					
			[19]		[20]		[21]	
			1*	2*	1*	2*	1*	2*
$H_6T^+ \rightleftarrows H_4T^- + 2H^+$ $p(K_{base} \cdot K_1)$	$\geqslant NH^+$ и $-SO_3H$	~ -2**	—	—	—	—	—	—
$H_4T^- \rightleftarrows H_3T^{2-} + H^+$ pK_2	$-SO_3H$	~ 4	—	2,3?	—	3,7	—	3,36
$H_3T^{--} \rightleftarrows H_2T^{3-} + H^+$ pK_3	$-AsO(OH)_2$	~ 8	2,3	5,8?	3,7	8,4	3,36	7,92
$H_2T^{3-} \rightleftarrows HT^{4-} + H^+$ pK_4	$-AsO_2OH^-$	$\sim 11,5$	5,8	11,7	8,4	11,8	7,92	—
$HT^{4-} \rightleftarrows T^{5-} + H^+$ pK_5	$-OH$	~ 14	11,7	—	11,8	—	—	—

* pK according to the authors of the papers cited; 2) pK values on the basis of the present work.

** $p(K_{base} \cdot K_1) = 2(pH)_{50\%}$

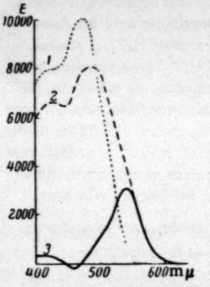


Fig. 4. Light absorption curves of the solutions: 1) Thoron in 0.1 M HCl, reference solution-water; 2) compound of sexivalent uranium with thoron at pH 4 (urotropine buffer solution). Measurement carried out relative to water; 3) compound of uranium with thoron at pH 4, relative to thoron solution.

Table 3. In Table 3 is given the most probable interpretation of the successive dissociation constants of thoron, as determined in the work described here, and derived on the basis of other results. The values quoted by other authors are included for comparison [19-21].

As is evident from Table 3, it is only possible here to give an evaluation of the product of the basicity constant ($K_{bas.}$) and the first acid dissociation constant of thoron (K_1): $K_{bas} \cdot K_1 = 10^2$. On the basis of the results given, it is not possible to give an evaluation of their separate values. Such an evaluation is possible for the remaining acid dissociation constants of thoron.

On the basis of the number of forms of thoron which have been determined in the present work, and the indices of its successive dissociation constants, it is suggested that the pK values proposed by other authors—interpreted by these authors as the first pK's of the dissociation of the arsonic group—are in fact shifted by one degree and are the pK's for the dissociation of the second sulfonate group. It follows from Table 3 that if this is the case, the results of Byrd [21] and Margenum [20] agree with the values found in the present work. The first two constants calculated by Adamovich and Didenko [19] differ by two degrees, while the third also agrees with the value established in the present work. The dissociation constants given here are concentration constants and refer to solutions containing 0.1-1 M salt.

2. The Interaction of Sexivalent Uranium and Thoron

As pointed out by Kuznetsov [1, 2], sexivalent uranium interacts with thoron in an acetic acid medium to give raspberry color. He established that 2 mg of uranium does not interfere with the determination of thorium in 0.3 M hydrochloric acid. Thomason et al [4] have pointed out variations in the influence of uranium during the determination of thorium, when the pH of the solutions is varied from 0.4 to 1.25.

TABLE 4

Electrochromatography of the Compound of Sexivalent Uranium with Thoron

Expt. No.	Medium	Concentration, M		Displacement of spot center		
		uranium	thoron	material	direction	rate, cm/min
1	pH 2 0,01 *M* HCl	$4\cdot10^{-4}$	$4\cdot10^{-4}$	Thoron Uranium thoronate	to anode —	$+7\cdot10^{-3}$ $<0,3\cdot10^{-3}$
		-		Thoron	to cathode	$-7\cdot10^{-3}$
2	pH 2 0,01 *M* HCl	$4\cdot10^{-4}$	$20\cdot10^{-4}$	Thoron Uranium thoronate	to anode —	$+13\cdot10^{-3}$ $<0,3\cdot10^{-3}$
3	pH 4 Urotropine buffer solution	$4\cdot10^{-4}$	$4\cdot10^{-4}$	Uranium thoronate	—	$<0,3\cdot10^{-3}$
4	pH 8 Ammoniacal buffer solution	$4\cdot10^{-4}$	$4\cdot10^{-4}$	Uranium thoronate	to anode	$+9\cdot10^{-3}$

Note. Experiments 1-3 lasted one hr; while experiment 4 took half an hour; voltage 500 v.

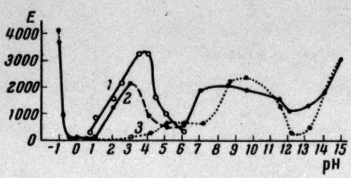


Fig. 5. Effect of pH on the light absorption of thoron and its compound with sexivalent uranium. 1) Uranium 10^{-3} M, thoron 1.8×10^{-4}M; urotropine buffer pH 1-6, λ = 545 mμ; 2) uranium 4×10^{-4} M, thoron 3×10^{-4} M, acetate buffer pH 3-6, λ = 545 mμ; 3) thoron solution, λ = 540 mμ.

The absorption curves of thoron and of the compound which this reagent forms with sexivalent uranium are shown in Fig. 4. The biggest difference between thoron itself and its compound with uranium is observed at 545 mμ; this is similar to that observed for the compounds formed between thoron and quadrivalent cations [4, 6, 10-12]. All optical density measurements were subsequently carried out relative to a thoron solution with the same total concentration. Thus, in all cases, the color of the unreacted reagent was subtracted, while the optical density measured was determined by the light absorption of the compound of thoron with sexivalent uranium alone. Although the light absorption of the compound thereby decreases, it is still always proportional to the concentration of the compound, independently of the ratio of uranium to thoron taken.

The relationships between the light absorption of thoron and of its compound with uranium and the pH are compared in Fig. 5. The biggest difference in color between thoron and its uranium compound is observed at pH 4 (an urotropine buffer solution). In an acetate buffer, the color of the compound is significantly weaker. During visual observation the following color changes are observed: in concentrated acid, raspberry; in dilute acid, the orange color of the reagent; at pH 4, raspberry; at pH 6, yellow; at pH 8-9, red; at pH 12 yellow; and in concentrated alkali back again to the raspberry color of the sexivalent uranium compound.

Using the method of isomolar series (Fig. 6), it was established that uranium reacts with thoron in a molar ratio of 1 : 1. The molar light absorption coefficient of the compound of uranium with thoron at a wavelength of 545 mμ is 3200 (see Fig. 4), after subtracting the light absorption of thoron itself.

As noted already the reference solution used in all the measurements was a thoron solution with the same concentration. For calculating the points in Fig. 7 and the results in Table 4, the uranyl thoronate concentration was determined by means of the formula

$$[UO_2H_{4-x}T] = \frac{D_{545}}{E_{545}\cdot l} = \frac{D_{545}}{3200\cdot l}.$$

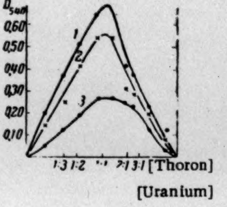


Fig. 6

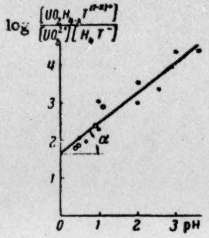


Fig. 7

Fig. 6. Composition of the uranium compound with uranium by the isomer series method. λ = 545 mμ. Cuvette 1.0 cm. 1) pH 4, uranium + thoron 8 × 10^{-5}M; 2) pH 4, uranium + thoron 6.5 × 10^{-5}M; 3) pH 2, uranium + thoron 6.5 × 10^{-5}M.

Fig. 7. The relation between log $\dfrac{[UO_2H_{4-x}T^{(1-x)+}]}{[UO_2^{2+}][H_4T^-]}$ and pH. •) points according to results of Thomason et al.[4]. The straight line was drawn by the method of least squares [27]: y = 1.6 + 0.8 pH, tangent α = 0.8 to about 1.

The uranyl and thoron concentrations were calculated by difference.

Presumably, uranium reacts with thoron according to the following scheme:

$$UO_2^{2+} + H_4T^- \rightleftarrows UO_2H_{4-x}T^{(1-x)+} + x\cdot H^+;$$

here H_4T^- is the thoron ion at pH 0-3, x is the number of ions in thoron replaced by uranium. Since the equilibrium constant of the reaction $K_{equilib.}$ is equal to:

$$K_{eq} = \frac{[UO_2H_{4-x}T^{(1-x)+}]\,[H^+]^x}{[UO_2^{2+}]\,[H_4T^-]},$$

then by taking logarithms and transforming this equation, we get

$$\lg\frac{[UO_2H_{4-x}T^{(1-x)+}]}{[UO_2^{2+}]\,[H_4T^-]} = \lg K_{eq} + x\cdot pH$$

In Fig. 7 is given the straight line constructed on the basis of points on Curve 1, Fig. 5, and some other data, over the pH range 0.4-3.5. This straight line can be described by the last equation. The slope of the straight line in Fig. 7 permits the coefficient x to be determined. We find in this way that x is about 1. From this it follows that the interaction of sexivalent uranium with thoron is of the type:

$$UO_2^{2+} + H_4T^- \rightleftarrows UO_2H_3T + H^+$$

It follows from this scheme that the compound formed in weakly acid solutions is electrically neutral. To confirm this we carried out some electrochromatographic experiments on the uranium compound at various pH's. When the experiments were complete the uranium was located on the paper sheet by means of potassium ferrocyanide; transfer of thoron and the compounds was observed visually. The experimental results are given in Table 4. As is evident from experiments 1-3, the compound of uranium with thoron hardly migrates at all and appears to be electrically neutral, since the transport velocities in the electrical field of the reagent itself (experiments 1 and 2) and of the cation UO_2^{2+} (experiment 1 — low pH and insufficient thoron) are considerably greater (1-2 orders at least).

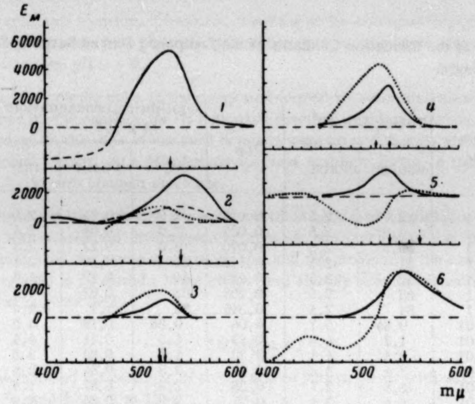


Fig. 8. Light absorption curves of thoron and of the compound of uranium with thoron at various pH's. 1) pH 1; 2) pH 4; 3) pH 6; 4) pH 9.5; 5) pH 12; 6) pH 15. ···· Thoron; —— uranium compound; --- the uranium compound in an acetate buffer solution.

During observations of solutions of sexivalent uranium and thoron at ratios greater than 1 : 4, it was observed that an orange precipitate is formed after 24 hr in media with pH from 2 to 6. In order to determine its composition, a solution with a pH of 4 was prepared (urotropine buffer solution) in which the concentrations of sexivalent uranium and thoron were 8×10^{-4} M and 4×10^{-4} M respectively. After removal of the precipitate on the next day, analysis of the decanted solution showed that the uranium concentration as found by the luminescent method was 3×10^{-4} M, while the uranium thoronate concentration was found to be 5×10^{-5} M by a spectrophotometric method. Consequently, the ratio of uranium to thoron in the precipitate is $5 \times 10^{-4} : 3.5 \times 10^{-4} = 1.4 : 1$ or about 1.5 : 1. Presumably, formation of the precipitate is connected with the formation of a sparingly soluble salt of sexivalent uranium thoronate with excess uranium, in which hydrogen ions are expelled from the sulfonate or arsono group.

The absorption curves of the various forms of thoron and of its compound with uranium at certain pH's are compared in Fig. 8. In strongly acid solutions the light absorption curves do not differ from each other, either in the presence or absence of uranium. Curves 1 and 2 in Fig. 5 show that at pH 1-3 formation of a compound between sexivalent uranium and thoron occurs. The weakening of the color at pH's between 4 and 6, as follows from Kuznetsov's hypotheses [26], is connected with a change in the state of the uranium bond in the compound, e. g., with the phenol hydroxyl. In an acetate medium, however, over the same pH range, competitive formation of acetate complexes of uranium may occur (Curve 2, Fig. 5).

On increasing the pH further, the color changes for the compound of uranium with thoron are reminiscent of the corresponding changes for thoron itself (Curves 2 and 3, Fig. 5), although, as is evident from Fig. 8, the absorption curves of the solutions do not completely coincide at equal pH values. Formation of uranate precipitates was not observed even in strongly alkaline media. It is obvious that under such conditions soluble alkaline salts of uranium thoronate are formed. This is confirmed by the electrochromatography of the compounds at pH 8 (Table 4).

The assumption that the change in the color of the compound which occurs on increasing the pH above 4 is related to changes in the composition of the compound does not receive much support from the experimental results. Uranium and thoron were mixed together in approximately equimolar amounts, the following results therefore do not support such an assumption: when the compound was examined electrochromatographically in a solution with pH 8, only one band was observed for the compound (Table 4); no separate bands for uranium

TABLE 5

Calculation of the Formation Constants of the Compound Formed Between Sexivalent Uranium and Thoron

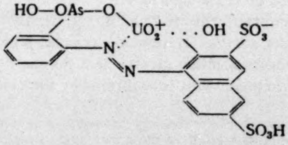
№	[H+] M	Taken, M × 10^4		D_{546}	Equilibrium concentrations, M × 10^4			K_{equil}
		uranium	thoron		UO_2^{2+}	UO_2H_3T	H_4T^-	
1	0,1	2,0	2,5	0,012	2,0	0,04	2,5	8
2	0,1	3,0	2,5	0,025	2,9	0,08	2,4	11
3	0,1	9,5	2,5	0,070	9,3	0,22	2,3	10
4	0,1	21	2,5	0,120	21	0,38	2,1	9
5	0,1	42	2,5	0,220	41	0,69	1,8	9
6	0,1	63	2,5	0,295	62	0,92	1,6	9
7	0,1	84	2,5	0,345	83	1,1	1,4	12
8	0,01	0,85	5,7	0,06	0,66	0,19	5,5	5
9	0,01	1,7	4,8	0,13	1,3	0,41	4,4	7
10	0,01	2,4	4,1	0,20	1,8	0,63	3,5	10
11	0,01	3,1	3,4	0,27	2,3	0,84	2,6	14
12	0,01	3,8	2,7	0,28	2,9	0,87	1,8	17
13	0,01	4,4	2,1	0,27	3,6	0,84	1,3	18
14	0,01	4,9	1,6	0,25	4,1	0,78	0,8	25
15	0,01	5,5	1,0	0,13	5,1	0,41	0,6	18
16	0,01	6,0	0,5	0,03	5,9	0,10	0,4	4
				Mean (confidence level 0.95).				11±9

and thoron were observed. The absence of uranate precipitates in strongly alkaline solutions also testifies to the absence of any changes in composition.

The reaction constant for the formation of the compound of sexivalent uranium with thoron, according to the scheme advanced above, can be determined by means of Fig. 7. The intercept made by the straight line on the ordinate is numerically equal to the free term in the equation for the straight line: log $K_{equilib.} = 1.6$ and $K_{equilib.} = 40$. The constant of this reaction can also be calculated on the basis of the results of the other series of spectrophotometric measurements given in Table 5.

As is evident from the Table, the mean value of $K_{equilib.}$ is almost the same as that determined by means of Fig. 7. The constancy of $K_{equilib.}$, when determined on the basis of the results of different series of measurements, confirms the scheme advanced for the reaction leading to the formation of the compound of sexivalent uranium with thoron at pH 0.4-3.5. The general value is $K_{equilib.} = 25 \pm 15$.

If the treatment adopted above of explaning the changes in light absorption with changes in pH is true, then, according to Curve 2, Fig. 5, it should be possible,on the basis of the points corresponding to the pH for a 50% color, to evaluate the indices of the acid dissociation constants of uranium thoronate $H_3(UO_2T)$. The following structural formula can be advanced for it:



The indices of the acid dissociation constants were found to be approximately equal to: pK_1 about 6.5 (sulfonate group); pK_2 about 11.5 (arsono group), and pK_3 about 14 (phenolic hydroxyl). They can be compared with the respective indices for the thoron constants: pK_2 about 4, pK_3 about 8, pK_4 about 11.5, and pK_5 about 14. The values of the last two constants coincide. Obviously, the state of the corresponding groups, i. e., the state of one hydroxyl of the arsono group and of the phenolic hydroxyl in uranium thoronate differ very little from their states in thoron itself, when the pH is > 6.

Thus, the effect of pH on the color of the compound formed between sexivalent uranium and thoron at pH 0.4-3.5 is well described by the equation for its formation reaction (uranium: thoron = 1 : 1). At pH 4-6, presumably, there is a change in the state of the bond between uranium and thoron, while at higher pH's, acid dissociation of the compound occurs. At a pH of about 4, excess uranium forms a sparingly soluble compound (uranium : thoron = 1.5 : 1) with uranium thoronate.

It should be pointed out that although the work described here does supplement existing information on the interaction of cations with o-arsono-o'-hydroxyazo compounds, the problem of the nature of the bonds between uranyl—and other cations—and the arsono and azo groups, and the problem of the changes with occur on increasing the pH, still remain to be solved. Ideas which have already been published [26] are only in partial agreement with the results given here.

SUMMARY

A study has been made of the behavior of thoron and of its compound with sexivalent uranium when the pH of the solution is changed from -1 to 15.

Six forms of thoron have been identified by a spectrophotometric method. It has been shown by means of electrochromatography that thoron is positively charged in concentrated acid, while at pH $\geq$ 0 it is negatively charged. The values of the successive dissociation constants of thoron have been established: $pK_2 \sim 4$, $pK_3 \sim 8$, $pK_4 \sim 11.5$, $pK_5 \sim 14$.

Formation of compound between sexivalent uranium and thoron starts at pH 0.4. The maximum color is observed at pH 4. Uranium reacts with thoron in the molar ratio of 1 : 1, one atom of hydrogen being thereby displaced. This compound has been shown to be electrically neutral by electrochromatography. The reaction constant of its formation at pH 0.4-3.5 is 25 ± 15. The values of the acid dissociation constants of uranium thoronate have been established at pH > 6: $pK_1 \sim 6.5$, $pK_2 \sim 11.5$, $pK_3 \sim 14$.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 17. 8,8'-DIQUINOLYLDISULFIDE- A NEW SELECTIVE REAGENT FOR THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER*

Yu. A. Bankovskii, A. F. Uevin'sh, E. A. Luksha,
and P. Ya. Bochkans
Institute of Chemistry, Academy of Sciences, Latvian SSR, Riga

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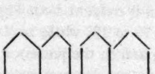
Despite the large number of methods already published for the determination of copper, determination of small amounts of this element is still one of the pressing problems of analytical chemistry. Apart from its marked tendency to form complexes, copper can also be readily converted into its univalent from which has strong reducing properties. The reducing properties of cuprous ions can be used for the analytical determination of copper, particularly when the reagent produced during the reduction forms (during the second phase of the reaction) an intensely colored or a sparingly soluble compound with copper.

A reagent which answers these requirements is 8,8'-diquinolyldisulfide (subsequently referred to as disulfide) which is obtained by the oxidation of 8-mercaptoquinoline**



We have established previously that cuprous ions reduce disulfide to 8-mercaptoquinoline, copper 8-mercaptoquinolinate with the structure indicated in [1] being subsequently formed.

A very selective method for the detection of copper on the basis of the formation of the complex mentioned above has been described previously [2]. The highly selective method described here for the quantitative determination of copper can be regarded as belonging to the class of so-called "in situ nascendi" reagent methods [3], and has the advantage that the 8-mercaptoquinoline which is formed during the reaction reacts with copper in strictly equivalent amounts. This also accounts for the high selectivity of the method suggested; as we have shown [4], the selectivity is incomparably less if excess thiooxine (8-mercaptoquinoline) is used, even in presence of powerful masking agents.

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* For Communication 16, see Izvestiya Akad. Nauk Latv. SSR, No. 1, 97 (1960).

** For the synthesis of 8-mercaptoquinoline and 8,8'-diquinolyldisulfide see Bankovskii, Ievin'sh, and Luksha [5].

Masking agents (usually tartrates) have to be used in the new method, mainly in cases where it is necessary to keep in solution those metal salts (Sb, Bi, Ti, Fe, Cr, etc) which readily hydrolyze in very weak acid or alkaline media.

Extractability of the Copper Complex as a Function of the pH of the Medium and the Nature of the Reducing Agent

A 0.2% solution of disulfide in chloroform, which is, at the same time, the best extractant for copper 8-mercaptoquinolinate, was used in all the experiments described below. When a 0.2% chloroform solution of disulfide was used, only a small amount of it was consumed—lost to the aqueous phase; it was found, however, that when a lower concentration was used, the copper was not completely extracted. The pH range for the extraction of the copper complex was determined when ascorbic acid and hydroxylamine hydrochloride were used as the reducing agents; the pH range was also determined in the absence of reducing agents, using the theoretical amount of thiooxine (the sodium salt $C_9H_6NSNa \cdot 3H_2O$ [5] was used). In order to keep the conditions constant, and to eliminate secondary factors as far as possible, the volume of the aqueous phase was kept at 50 ml both in these experiments and in all subsequent experiments. To 40 ml of buffer solution with a known pH, and contained in a separating funnel (150 ml) was added a solution (5 ml) containing 50 μg of copper; 5 ml of the reducing solution (a 20% ascorbic acid solution of a 50% hydroxylamine hydrochloride solution neutralized beforehand to the pH of the buffer being used) was then added, followed by 10 ml of the 0.2% chloroform solution of disulfide. After vigorous shaking for 3-4 min, the brown chloroform extract of copper 8-mercaptoquinolinate was separated, filtered through a plug of cotton wool, and its optical density measured in a FÉK-M photocolorimeter, using a 1 cm cuvette and a blue filter. The percentage copper extracted was calculated by means of a calibration curve constructed beforehand, in almost neutral solutions of copper using excess 8-mercaptoquinoline. As is evident from Fig. 1 (Curve 2), when ascorbic acid is used, copper is completely extracted over the pH range 2.19 to 13, while in the presence of hydroxylamine it is completely extracted over the range 4 to 11.5 (Curve 3), and in the presence of the theoretical amount of thiooxine over the range 2 to 14 (Curve 1). Ascorbic acid permits the determination of copper in more acid solutions; this is very important, particularly during the determination of copper in salts which readily hydrolyze. It was observed, however, that ascorbic acid also slowly reduces the disulfide to 8-mercaptoquinoline. In the presence of very high concentrations of certain metals (particularly Fe, Ni, and Co), during prolonged extraction, these metals pass into the extract. This occurs to a considerably smaller extent when hydroxylamine is used as the reducing agent.

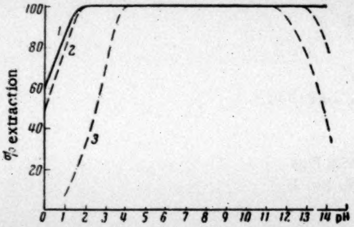

Fig. 1. The relation between the extractability of copper 8-mercaptoquinolinate and the pH of the medium and the nature of the reducing agent. 1) The theoretical amount of 8-mercaptoquinoline; 2) disulfide in the presence of ascorbic acid; 3) disulfide in the presence of hydroxylamine. a) % extraction.

The Sensitivity of the Method and Conformity of the Chloroform Extracts to Beer's Law. In order to study the conformity of the chloroform extracts of copper 8-mercaptoquinolinate to Beer's law, the reaction was carried out in solutions buffered with sodium acetate (pH 5-6). In view of the wide pH range over which copper 8-mercaptoquinolinate is extracted (pH 2-12) strict observation of the pH value is not important. The optical density of the extract, after filtration through cotton wool, was measured in a 1 cm cuvette on a SF-4 spectrophotometer at 432 mμ, or in a FÉK-N-54 photocolorimeter with a violet filter. The reference solution was an extract obtained in the same way but in the absence of copper. All the reagents used were carefully purified from copper as described below. As is evident from Fig. 2, chloroform solutions of copper 8-mercaptoquinolinate conform to Beer's law up to 8 μg Cu in 1 ml of chloroform when the measurements are made on a FÉK-N-54 photocolorimeter. At higher copper concentrations, the calibration curve deviates slightly from linearity. In practice, copper can be determined in concentrations up to 13 μg of Cu in 1 ml of chloroform.

TABLE 1

Determination of Copper in Pure Solutions

Cu taken, μg	Cu found, μg				Mean error, %
5	5,1	4,8	4,9	5	−1
20	19	20,5	21	21,5	+2,5
50	49	51	50	50	0
100	98	100	99	97	−1,5

The molar extinction coefficient of chloroform solutions of the copper complex at 432 mμ is 9500 [1].

Determination of Copper in Pure Solutions. In view of the wide pH range within which copper 8-mercaptoquinolinate can be extracted, copper can be determined in both acid and alkaline solutions. The possibility of varying the reaction conditions over a wide range is a very important advantage of this method of determining copper. It means, for example, that copper can be determined in ammoniacal solutions in the presence of appreciable amounts of the platinum metals; such a determination cannot be carried out in acid solutions. After acid decomposition the test solution is usually acid.

The greater part of the acid can be conveniently neutralized with sodium acetate. Alkaline and ammoniacal solutions are only to be recommended in the presence of predominating amounts of the platinum metals and other metals which exist in alkaline media in a stable anionic form.

The experiments described blow for the determination of copper in pure solutions were carried out in a weakly acid medium at pH 5-6. The experimental procedure was the same as that used for construction of a calibration curve. As the results in Table 2 show, varying amounts of copper can be determined with an error from -1.5 to +2.5%. Such an accuracy is quite adequate for the determination of small amounts of copper.

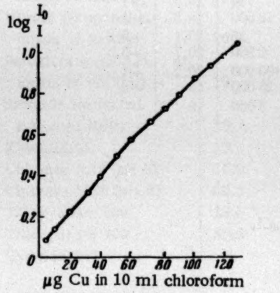

Fig. 2. Conformity of chloroform extracts of copper 8-mercaptoquinolinate to Beer's law (FEK-N-54 photocolorimeter, violet filter).

Determination of Copper in the Presence of Other Elements. Reagents: 1) 0.2% solution of disulfide in chloroform* . The solution is stored in the dark. It is desirable that the disulfide solution should not be kept for more than two weeks, and should be stored in a bottle covered with black paper; 2) 50% hydroxylamine hydrochloride solution; 3) 20% ascorbic acid solution; 4) 50% sodium acetate solution; 5) 20% sodium tartrate solution, ammonia, NaOH solution, and acid.

Purification of Reagents. All reagents used should be carefully purified from copper, and this can be done as follows. To 200-300 ml of sodium acetate or tartrate contained in a separating funnel is added 5 ml of hydroxylamine hydrochloride solution, and any copper is extracted with 2-3 portions of 30-40 ml of the chloroform solution of disulfide until the extract is colorless. Hydroxylamine hydrochloride and ascorbic acid solutions which have been neutralized to pH 4 are purified (when necessary) in a similar way. Hydroxylamine and ascorbic acid solutions with a pH 4 are unstable and should be prepared daily. It is best therefore to use high purity preparations (free from copper) so that there is no need for purification. Ammonia and the acids required are distilled. NaOH solutions can be freed from copper in this way as long as their concentrations are not higher than 0.5 N.

20-30 ml of test solution (hydrochloric, nitric, sulfuric acid solutions, etc, see Note 1) is placed in a 150 ml separating funnel and is neutralized with alkali to pH 1-2; sodium acetate is then added until the pH is 5-6

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* The 8,8'-diquinolydisulfide should dissolve in chloroform to give a colorless solution. When a yellow or brownish colored solution is obtained, it is purified as follows. Ten g of 8,8'-diquinolyldisulfide is dissolved in 20 ml of concentrated hydrochloric acid and 5 g of sodium hypophosphite added. The solution is boiled for 5 min, cooled, diluted with water to 200 ml, and neutralized with sodium carbonate solution to a pH of 5. A bright-red crystalline precipitate of thiooxine dihydrate $C_9H_7NS \cdot 2H_2O$ separates out; the latter is purified from heavy metals as described in the paper by I. A. Shevchuk and E. A. Luksha [Izvest. Akad. Nauk Latv. SSR, No. 2, 127 (1961)]. The purified thiooxine dihydrate is converted into the disulfide by the method described in the paper cited.

TABLE 2

Determination of Copper in the Presence of Other Elements (20 μg copper was present in a final volume of 50 ml)

Foreign element (me), mg	Ratio Cu/me	Cu found, μg	Error, %	Foreign element (me), mg	Ratio Cu/me	Cu, found, μg	Error, %
Fe^{2+} 1100	1 : 55 000	20,8	+4	In^{3+} 280*	1 : 14 000	20	0
Ni^{2+} 4000	1 : 200 000	20,2	+1	Th^{4+} 500*	1 : 25 000	20	0
Co^{2+} 1500	1 : 75 000	20	0	La^{3+} 300*	1 : 15 000	20,2	+1
Cd^{2+} 2000	1 : 100 000	19,5	−2,5	Zr^{IV} 1000	1 : 50 000	19,8	−1
Mn^{2+} 2000	1 : 100 000	20,1	+0,5	Os^{VIII} 7,5	1 : 375	19,6	−2
Mo^{VI} 5000	1 : 250 000	20	0	Ru^{III} 5	1 : 250	19,7	−1,5
Bi^{3+} 2000	1 : 100 000	19,4	−3	Pt^{IV} 15**	1 : 750	20	0
Sb^{3+} 3000	1 : 150 000	19,6	−2	Pt^{IV} 3	1 : 150	19,9	−0,5
W^{VI} 5000	1 : 250 000	20,3	+1,5	Ta^{V} 40*	1 : 2 000	20,7	+3,5
Cr^{3+} 1300	1 : 65 000	20,1	+0,5	Nb^{V} 7,5*	1 : 375	20,1	+0,5
Pb^{2+} 6000	1 : 300 000	20	0	Ti^{IV} 800	1 : 40 000	19,5	−2,5
Tl^{+} 1000	1 : 50 000	20	0	Ge^{IV} 1000	1 : 50 000	20	0
Sn^{IV} 5000	1 : 250 000	19,8	−1	Te^{IV} 3	1 : 150	20,2	+1
As^{III} 600	1 : 30 000	20,2	+1	Hg^{2+} 250***	1 : 12 500	19,8	−1
As^{V} 2000	1 : 100 000	20	0	Se^{IV} 0,5	1 : 25	20,1	+0,5
V^{V} 300	1 : 15 000	20,2	+1	Pd^{2+} 50**	1 : 2 500	20,7	+3,5
Zn^{2+} 4000	1 : 10 000	19,5	−2,5	U^{VI} 2000	1 : 100 000	20,2	+1
Al^{3+} 1000	1 : 50 000	20,1	+0,5	Ag^{+} 560***	1 : 28 000	19	−5
Mg^{2+} 2000	1 : 100 000	19,5	−2,5	Rh^{III} 60*	1 : 3 000	19	–
Ga^{3+} 500*	1 : 25 000	20	0				
Re^{VII} 10*	1 : 500	20,3	+1,5				

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* The limiting permissible amount was not established.

** In an ammoniacal medium at pH 8-9 in the presence of NH_4Cl.

*** In the presence of KI.

(see Note 2). Five ml of hydroxylamine or ascorbic acid solution is added (see Note 3), and the copper is extracted with 5 or 10 ml of the chloroform solution of disulfide, by vigorous shaking for 3-4 min. The yellow-brown extract is filtered through a plug of cotton wool, and the optical density measured in a 1 cm cuvette on a spectrophotometer at 432 $m\mu$, or on a photocolorimeter with a blue or violet filter. The amount of copper is determined by means of a calibration curve which has been constructed using pure solutions of copper and all the reagents mentioned above.

Notes: 1. As will be shown below, high concentrations of chlorides, sulfates, nitrates, and other anions do not affect the accuracy of copper determination. Consequently, aliquots of test material (minerals, ores, steels, alloys, etc) can be dissolved in any acid. Any oxidizing agents present in solution are removed by excess hydroxylamine or ascorbic acid solutions.

2. During the determination of traces of copper in iron, aluminum, antimony, bismuth, titanium, zirconium, chromium, germanium,etc.and their salts, sodium tartrate can be used for preventing their hydrolysis in solution at pH 5-7. It is best to add the 20% sodium tartrate solution to the acid test solution first, and only then adjust the pH to 5-6. When this procedure is adopted Sb, Bi, and Ti hydroxides,which are difficult to dissolve, are not precipitated. When germanium is present, tartrate is added to the alkaline solution of germanic acid, and the pH then adjusted to 5-6. When the tartrate concentration of the solution is very high (particularly in alkaline media) some of the copper is also complexed, but in a weakly acid medium (ph 4-5),3-4 ml of the 20% sodium tartrate solution in a total volume of the test solution of 50 ml does not affect the extraction of the copper. At pH 6-7, when the amount of tartrate mentioned above is present, copper extraction is slowed down somewhat; accordingly, in order to extract the copper completely,the time for which the extraction is carried out must be increased to 5 min.

TABLE 3

The Effect of Anions on the Accuracy of Copper Determination (20 μg of Cu was present in a volume of 50 ml; pH 5)

Anions, mg	Cu found, μg	Error, %
Oxalate 4	20.5	+2.5
Oxalate 1000(pH 8)	19.5	-2.5
Citrate 1320	20.3	+1.5
Tartrate 2500	20	0
Fluoride 80	21	+5
Iodide 7000	19.6	-2
Phosphate 3750	19.4	-3
Borate (saturated solution of $Na_2B_4O_7 \cdot 10 H_2O$	20.2	+1
Sulfate (saturated solution of Na_2SO_4)	20	0
Nitrate (saturated solution of $NaNO_3$)	20.5	+2.5
Perchlorate (saturated solution of $NaClO_4$)	19	-5
Bromide (saturated solution of NaBr)	19.7	-1.5
Thiosulfate	19	-5
Chlorate 0.39 (pH 5)	19.2	-4
Chlorate 5000 (pH 8)	20.3	+1.5
Thiocyanate 500	18.5	-7.5
Thiocyanate 100	19.2	-4
Cyanide 500	0	-100

When very large amounts of iron are present, 5 ml of the 20% tartrate solution is used, since when such amounts are present iron tartrate is precipitated and this interferes with extraction of the copper and removal of the extract. Large amounts of iron (1100 mg) slow down extraction of copper to some extent, so that the duration of the extraction should be increased to 5 min. Citrates readily keep Sb, Bi, Ti, and Fe in solution, but hinder extraction of copper to some extent, and they cannot therefore be recommended for this purpose.

In order to determine traces of copper in metallic antimony, bismuth, or their salts, 10 g of the salt is dissolved on heating in 50 ml of a 15% sodium tartrate solution having a pH of 5-6. A clear solution is obtained, from which copper is quantitatively extracted as indicated. In the given instance, this amount of tartrate does not interfere with extraction of copper in the presence of the amounts of antimony or bismuth indicated, since the main bulk of the tartrate is combined with these metals.

3. Apart from the amount of ascorbic acid or hydroxylamine solution taken for reducing copper to its univalent state, enough of these reducing agents should be taken to reduce all those components present in the solution (Fe^{3+}, CrO_4^{2-}, etc) which can be reduced by them. When small amounts of copper (2-3 μg) are present, it is best to use ascorbic acid, since hydroxylamine does not completely reduce copper in very dilute solutions (2-3 μg in 50 ml). As a consequence of this, the results may be 20% too low.

Limitation of the Method. Platinum Metals, Gold, Silver, and Selenium. Some of these elements (Pd, Ag, Au) are reduced to the elemental state by hydroxylamine in weakly acid solutions, or to lower valence states (Os, Ru). The sparingly soluble precipitates which are thereby formed entrain some of the copper. This is true for Pd, Pt, Au, Ag, and Se. Ho, Os, Ru, Rh, and Ir are not precipitated in weakly acid (pH 5-6) and neutral solutions, and do not interfere with determination of copper when they are present in moderate amounts. In general, formation of a solid phase in the test solution is not desirable, since under such conditions part of the copper is lost. It is different in an ammoniacal medium, whereby platinum, palladium, and selenium are not reduced at a pH of 8-9 in the presence of several grams of NH_4Cl. Under such conditions, it is possible to mask 50 mg Pd, 15 mg Pt, and 0.5 mg selenium.

Gold and silver, even when present in very small amounts, are reduced by ascorbic acid to the elemental state, and entrain appreciable amounts of copper. Gold and silver can be complexed into very stable complexes by means of thiosulfate in an ammoniacal medium, and the gold and the silver in these complexes are not reduced by hydroxylamine and ascorbic acid. Thiosulfate ions, however, also complex copper so that very low results are obtained for the latter. Potassium iodide is a strong masking agent for silver and mercury. 20-30 ml of 50% KI solution can mask 560 mg silver and 250 mg mercury. In the presence of this amount of mercury extraction should not be carried out for more than 4 min.

Effect of High Concentrations of Other Elements. As mentioned above, when a spectrophotometer is used, the minimum amount of copper which can be reliably determined (with an error of 5-7%) is 2 μg. The reaction is slightly less sensitive than other methods, e. g., the dithizone or diphenylcarbazone methods. In this connection, during the determination of very small amounts of copper in pure metals, of particular importance is the fact that it is possible to take large aliquots of test metal. When certain foreign metals are present in large amounts in the solution, difficulties may arise either as a result of hydrolysis, or sometimes as a result of transfer of the metal (Fe, Co, Ni) into the extract following upon substitution of the copper in the 8-mercaptoquinolinate.

TABLE 4

Determination of Copper in Synthetic Mixtures (20 and 100 μg Cu taken in a total volume of 50 ml of test solution)

Foreign element, mg	Cu found, mg	Error, %
Sb—50, Bi—50, Mo—50, Ti—3, Zr—20, Fe—20, Pb—50, Zn—30	20,1	+0,5
	98,1	−1,3
Co—10, Mn—50, Zn—50, V—20, Cd—20, Fe—50, Zr—50, Cr—20	20,2	+1
	100	0

Magnesium does not react with 8-mercaptoquinoline, but at high magnesium salt concentration, at pH 5-6, as a result of partial hydrolysis, basic salts are formed which interfere with separation of the extract. Ammonium chloride can usually be used for preventing hydrolysis in this case. Five g of NH_4Cl should be used for a solution containing 2 g Mg.

Aluminum. Determination of traces of copper in large aliquots of aluminum must be carried out at pH 4, since at pH 5-6 the aluminum salts hydrolyze to an appreciable extent. Sodium tartrate can be used for preventing precipitation of the basic salts, but when large amounts of the former are used, as mentioned already, extraction of copper is slowed down to some extent.

Nickel and Cobalt, too, in relatively moderate amounts (e. g. 50 mg), in the presence of large amounts of iron, color the solution rose when extraction is carried on for a long time (5-6 min). Nevertheless, traces of copper can be determined in the presence of large amounts of nickel and cobalt against a background of iron, as long as the extraction is only carried out for not more than three minutes, and the extract is removed immediately.

TABLE 5

Coprecipitation of Copper Thiooxinate with 8,8'-Diquinolyldisulfide

Disulfide, mg	Cu taken, μg	Cu found, μg	Disulfide mg	Cu taken, μg	Cu found, μg
50	12,7	13,2	10	12,7	12,7
50	—	~ 1	10	—	~ 1
25	12,7	12,8	5	12,7	12,0
25	—	~ 1	5	—	~ 1

TABLE 6

Coprecipitation of Copper from Solutions of Cobalt and Manganese Salts by Means of 8,8'-Diquinolyldisulfide

Metal, g in 300 ml	Cu taken, μg	Cu found, μg
Co^{2+} —15	5	4,5
Co^{2+} 15	5	4,9
Co^{2+} 15	5	4,8
Mn^{2+} —30	5	5,1
Mn^{2+} 30	5	4,4
Mn^{2+} 30	5	4,5

Tin and Titanium in their lower valence states (Sn^{II} and Ti^{III}) should be absent, since they vigorously reduce the disulfide to 8-mercaptoquinoline. Under these conditions tin forms a 8-mercaptoquinolinate which is extracted to give a yellow colored solution. Titanium does not form a compound with the reagent, but the 8-mercaptoquinoline formed reacts with many metals, as a result of which the reaction for copper loses its selectivity. In view of this, tin and titanium should be oxidized to the quadrivalent state by bromine, excess of which is removed by means of ascorbic acid or hydroxylamine. Sodium tartrate is used to prevent hydrolysis at pH 5-6.

The other elements in the amounts indicated in Table 2 do not lead to difficulties during the determination of copper.

Effect of Anions. Cyanides and thiocyanates should be absent; small amounts of oxalates (at pH 8 and higher, oxalates do not interfere), thiosulfates and chlorates (the latter in acid solution) can be tolerated. In alkaline media, chlorate ions like other oxidizing anions, do not interfere even in saturated solutions.

Table 3 contains the results for the determination of copper in the presence of various anions.

Determination of Copper in Synthetic Mixtures. Copper has been determined in various synthetic mixtures by means of the analytical procedure described above. Sodium tartrate was used for preventing the precipitation of several elements (the precipitation follows upon the hydrolysis of their salts). Table 4 contains some results for the determination of copper in synthetic mixtures.

The Use of 8,8'-Diquinolyldisulfide as a Selective Coprecipitant[*]. In order to determine very small amounts of copper in large volumes of solutions, when large aliquots of metals or their salts are taken, the copper must be concentrated beforehand. The disulfide,which is insoluble in weakly acid or alkaline aqueous solutions, and coprecipitates copper 8-mercaptoquinolinate, is a very selective coprecipitant for copper. The reagents used in the experiments described below were carefully purified from traces of copper. Copper was separated by coprecipitation as follows. To 500 ml of water containing a known amount of copper was added 10 ml of a 10% aqueous solution of ascorbic acid, 20 ml of a 20% solution of sodium acetate, and finally a solution of disulfide in pyridine with a concentration of 25 mg/ml. The disulfide precipitate plus the coprecipitated copper 8-mercaptoquinolinate were filtered off on a Gooch crucible fitted with filter paper. The crucible plus filter and precipitate were dried at 120° and the precipitate plus filter then transferred to a test tube, in which the precipitate (disulfide plus copper 8-mercaptoquinolinate) was dissolved in 5 ml of chloroform. The solution was filtered through a plug of cotton wool into a 1 cm cuvette, in which its optical density was measured on a SF-4 spectrophotometer at 432 $m\mu$. The amount of copper was determined by means of a calibration curve constructed beforehand. As is evident from Table 5, the results obtained were satisfactory. For complete coprecipitation of copper, one hour should elapse from the moment at which disulfide is added to the test solution.

Coprecipitation of gamma amounts of copper in the presence of foreign metals was carried out in the same way, but instead of a pyridine solution of disulfide, a dioxane solution of disulfide (6 mg/ml) was used, since at the moment when pyridine is added some of the foreign metals are precipitated as their hydroxides. The salt of the foreign metal was subjected to careful purification from copper by the same method. When high concentrations of heavy metals are present, part of the metals is precipitated as their 8-mercaptoquinolinates. Accordingly, the precipitate was dissolved in a mixture of concentrated hydrochloric acid and hydrogen peroxide. The copper content of the solution obtained was then determined colorimetrically by the method described above. The precipitate plus the filter was transferred to a beaker and dissolved on heating in a mixture of 1 ml of concentrated hydrochloric acid and four drops of concentrated H_2O_2. The completely clear liquid obtained was heated until all the H_2O_2 had decomposed, and was then transferred into a separating funnel. One ml of 20% ascorbic acid solution was added, followed by 25% sodium acetate solution until the pH was about 5. The total volume of the aqueous phase in the separating funnel was 7-8 ml. The copper was extracted with 5 ml of a 0.2% chloroform solution of disulfide. The extract was filtered through a plug of cotton wool, and its optical density measured in a 1 cm cuvette on a SF-4 spectrophotometer at 432 $m\mu$. The amount of copper was determined by means of a calibration curve. As is evident from Table 6, the experimental results can be regarded as satisfactory.

When 1 ml of the extractant solution is used (0.2% chloroform solution of disulfide) for extracting copper, it is possible to determine from 0.1 to 1 μg of copper by this method.

Hydroxylamine can be used instead of ascrobic acid as a reducing agent.

SUMMARY

A description is given of a photometric method for the determination of copper, which is based on the interaction of cuprous ions (in the presence of an excess of a reducing agent–hydroxylamine or ascrobic acid) with 8,8'-diquinolyldisulfide to form cuprous 8-mercaptoquinolinate $CuC_9H_6NS \cdot C_9H_6NSH$.

The reagent is a highly selective one for copper. Even in the absence of excess reagent, the reaction is quantitative over a very wide pH range of 2.19 to 13 in the presence of ascrobic acid, and from 4 to 11.5 in the presence of hydroxylamine; this is possible because of the high stability of the copper complex.

The sensitivity of the reagent does not change in the presence of several masking agents, e. g., tartrates, which can therefore be used for keeping in solution those salts which tend to hydrolyze readily in weakly acid and alkaline solutions.

The reaction is quantitative even in ammoniacal solutions (not more than 5 % NH_4OH) so that ammonia can be used in some instances keeping certain elements in solution in alkaline media.

Very large amounts of Fe, Ni, Co, Cd, Mn, Mo, Bi, Sb, W, Cr, Pb, Tl, Sn^{IV}, As, V, Zn, Al, Mg, Ga, Re, Zr, In, Th, La, Ti, the alkali and alkaline earths do not interfere with the determination of gamma amounts of copper. Pt, Ru, and Os ions can be tolerated in amounts which are 150-400 times that of copper, and Se ions in

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[*] The experimental work was carried out by L. M. Rengart.

amounts which are 25 times that of copper. Gold should be absent since it is reduced by ascorbic acid to the elemental state, and coprecipitates part of the copper.

High concentrations of most of the common anions (chlorides, bromides, iodides, fluorides, sulfates, phosphates, nitrates, chlorates, perchlorates, borates, and tartrates) do not affect the accuracy of copper determination. Thiocyanate interferes with extraction of copper to some extent; cyanide ions should be absent.

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DETERMINATION OF THE INSTABILITY CONSTANT OF THE COMPLEX OF BERYLLIUM WITH ETHYLENEDIAMINETETRACETIC ACID

L. P. Adamovich and I. N. Napadailo

A. M. Gor'kii Khar'kov State University

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There is no information in current textbooks [1] or in the periodical literature on the instability constant of the compound of beryllium with ethylenediaminetetracetic acid (EDTA-H_4Y). Pribil [2] has indicated that this complex is a very stable one, while some research workers have assumed that such a compound does not exist. The disodium salt of EDTA (EDTA-Na)—so called Complexon III—has already found wide application for the determination of beryllium, and is specified in a number of analytical procedures [3]. The absence of any information on $K_{inst.}$ of the compound of beryllium with EDTA renders these procedures empirical, and means that new procedures cannot be developed.

Attempts to use spectrophotometric methods both for determining beryllium by means of EDTA-Na [4], and for studying the interaction between beryllium and this reagent, were unsuccessful [5]. Our preliminary experiments showed that the maximum light absorption of both EDTA-Na and of its complex with beryllium lies in the far ultraviolet, which is not covered by apparatus such as the SF-4, while the descending sections of the curves, which are covered by the SF-4, do not differ enough from each other.

TABLE 1

Experimental Results Used for Calculating the Characteristics of the Exchange of H^+ ions for Be^{2+} ions. $\mu = 0.05$, $f_1 = 0.85$

g, e	V, ml	Initial conditions		Equilibrium conditions		
		pH°	$\overset{\circ}{c}_{Be} \cdot 10^3$/ml	pH	$c_1 \cdot 10^3$ M	$c_2 \cdot 10^3$ M
0,2	100	2,18	10	2,05	1,05	7,82
0,2	50	2,05	9	1,80	1,86	5,44
0,5	100	2,18	10	1,90	1,48	4,67
0,5	100	2,18	10	1,90	1,48	5,00
0,8	100	2,23	10	1,70	2,34	2,99
1,0	100	2,23	10	1,70	2,33	2,70
1,5	100	2,23	10	1,60	2,95	0,99

It was decided therefore to use an ion exchange method, the theory of which has been developed in sufficient detail [6]. We considered that it would be impossible to determine the composition of the compound formed, and assumed that it is 1 : 1, since we could not find a published reference to any other composition for divalent metals and comparatively dilute solutions.

We decided to work with fairly acid solutions (pH ≅ 2), in order to eliminate complications arising from hydrolysis of the Be^{2+} ion. Under these conditions, according to Schwarzenbach [7], the complex compounds formed are of the type $MeHY^-$. The problem therefore only consisted in determining the instability constant of the complex $BeHY^-$.

Reagents, Apparatus, Experimental Technique. The cation exchange resin KU-1, the H-form, was used; the particle size of this resin was 0.25-0.5 mm, it was washed and dried at 70° prior to use. Beryllium solutions were prepared from $BeSO_4 \cdot 4H_2O$ chemically pure grade, which had been recrystallized twice from water. The concentration of the stock solution was checked gravimetrically (precipitated as $Be(OH)_2$ and weighed as BeO).

The working solutions were prepared by dilution of the stock solution; their concentrations were established photometrically [8] on a FÉK-M apparatus; when the system contained EDTA-Na, its effect was eliminated, so that a determination in this case gave the sum of simple Be^{2+} ions and those ions complexed by ethylenediaminetetracetic acid. The EDTA-Na solution was prepared by dissolving an accurately weighed aliquot of the twice recrystallized commercial product $Na_2H_2Y \cdot H_2O$.

The initial value of the ionic strength of all the solutions was constant and equal to about 0.05, while the final value was about 0.04. The ionic strength was maintained constant by suitable selection of the initial concentrations of all the components of the system, not by adding an indifferent electrolyte. The values of the activity coefficients required for the calculations were taken from the textbook by Lur'e [9].

The pH values were measured with a glass electrode (with a tube amplifier) which had been calibrated against the hydrogen electrode.

The experimental temperature was 25 ± 1°.

Ion exchange was carried out under static conditions by mechanical agitation of an aliquot of the cation exchange resin with a known volume of the test solution for four hours—this time proved sufficient for equilibrium to be established. The amount of cation exchange resin taken did not exceed 1.5 g, while the volume of the solution was 100 ml in most cases; correction for swelling of the resin was negligible and was ignored.

Experimental Results. First of all it is necessary to determine the exchange constant of H^+ ions for Be^{2+} ions, ($K_{exchange}$), and the maximum capacity (α_m) of the KU-1 cation exchange resin for Be^{2+} ions. The ion exchange process can be represented thus:

$$HR + {}^1/_2Be^{2+} \rightleftarrows {}^1/_2BeR_2 + H^+.$$

Denoting the equilibrium content of H^+ and Be^{2+} ions in the adsorbent by α_1 and α_2 mg · equiv./100 g respectively, and the equilibrium concentration of the same ions in solution by c_1 and c_2 M respectively, and finally letting $K^{-1}_{exchange} = K'_{exchange}$, we get

$$a_1 = K'_{ex} \cdot \left(\frac{a_2}{c_2}\right)^{1/2} \cdot c_1. \tag{1}$$

Bearing in mind that the values c_1 and c_2 are experimental values, $\alpha_1 = \alpha_m - \alpha_2$, and in turn $\alpha_2 = (c^0_{Be} - c_2) \cdot V \cdot 200/g$, where c^0_{Be} is the initial beryllium concentration in solution (m), V is its volume (in ml), while g is the amount of cation exchange resin taken (in g), then rewriting (1);

$$a_2 = a_m - K'_{ex}\left(\frac{a_2}{c_2}\right)^{1/2} \cdot c_1, \tag{2}$$

it is evident that the unknown parameters in the equation for the straight line (2)— α_m and $K'_{exchange}$ —can be found either graphically or by the method of mean squares, from the experimental results.

The experimental results are given in Table 1. The most probable values of the exchange constant of H^+ ions for Be^{2+} ions and the maximum capacity of the KU-1 resin for Be^{2+} ions were found to be $K'_{exchange} = 11.5$ and $\alpha_m = 236$ mg · equiv./100 g respectively; these values were calculated from the experimental results by the method of least squares.

One can next proceed to determine the instability constant of beryllium ethlenediaminetetracetate, which, being an anion, is not absorbed by the cation exchange resin. A series of mixtures with a constant ionic strength, and known values of pH^0, c^0_{Be}, and $c^0_{Na_2HY}$ were shaken with a known amount of cation exchange resin. After equilibrium had been established, the new values of the pH and of c'_{Be} = total of complexed and uncomplex beryllium particles were determined, i. e.

$$c'_{Be} = [Be^{2+}]' + [\text{complexed}],$$

where $[Be^{2+}]'$ denotes the sum of all the beryllium particles which have not been complexed. From (1) we obtain:

$$c_2 = [Be^{2+}]' = (K'_0)^2 \cdot \left(\frac{c_1}{a_1}\right)^2 \cdot a_2. \tag{3}$$

TABLE 2

Results Used for Calculating $K_{instab.}$ for Beryllium Ethylenediaminetetracetate; $\mu \cong 0.05$; $f_1 = 0.85$; V=100 ml; g = = 0.5_g; $K'_{exchange} = 11.5$; $\alpha_m = 236$

$\overset{\circ}{c}_{Be} \cdot 10^3$ M	$\overset{\circ}{c}_{Na_2H_2Y} \cdot 10^3$ M	pH°	$c'_{Be} \cdot 10^3$ M	pH	$K_{instab.}$ 10
8,0	2,3	2,45	3,40	1,95	1,10
8,0	2,3	2,45	3,38	1,95	1,71
7,5	3,0	2,33	3,24	1,93	1,04
7,5	3,0	2,33	3,22	1,93	1,18
7,0	3,7	2,28	3,08	1,88	1,12
7,0	3,7	2,28	2,90	1,87	2,16
6,0	5,0	2,35	2,36	1,97	2,14
6,0	5,0	2,35	2,40	2;05	1,91

$K_{instab.} = (1,5 \pm 0,2) \cdot 10^{-9}$

This expression permits $[Be^{2+}]'$ to be calculated, since $K'_{exchange}$ is known, and $c_1 = [H^+]$ is found directly by experiment.

$$a_2 = \frac{(c^0_{Be} - c'_{Be})\, V \cdot 200}{g} \text{ and } a_1 = a_m - a_2.$$

The instability constant of the complex $BeHY^-$ was calculated by the formula:

$$K_{inst.} = \frac{[Be^{2+}]' \cdot \beta\, [HY^{3-}]' \cdot \alpha}{[BeHY^-]}, \tag{4}$$

where $[HY^{3-}]'$ is the sum of all the particles of EDTA-Na not bound as a complex; $[HY^{3-}]' = \overset{\circ}{c}_{Na_2H_2Y} - (c'_{Be} - c_2)$. The equilibrium concentration of the complex $[BeHY^-] = c'_{Be} - c^2$. The coefficient β is the fraction of Be^{2+} ions in the total of the uncomplexed beryllium particles. Taking into account the process [10]

$$Be^{2+} + H_2O \rightleftarrows BeOH^+ + H^+, \quad K_r = 2{,}32 \cdot 10^{-4}$$

an expression for β as a function of $[H^+]$ can be found:

$$\beta = \frac{[H^+]}{[H^+] + K_r}.$$

The coefficient α is the fraction of HY^{3-} ions in the total of all the uncomplexed particles of EDTA-Na. For a given pH it is calculated by means of the equation:

$$\alpha = \frac{1}{1 + \frac{[H^+]}{\varkappa_3} + \frac{[H^+]^2}{\varkappa_2\varkappa_3} + \frac{[H^+]^3}{\varkappa_1\varkappa_2\varkappa_3}},$$

in which $\alpha_1 \ldots {}_3$ are the constants for the stepwise acid dissociation of H_4Y [2]. The low pH value of 2 at which the work was carried out enables one to ignore the last fourth stage of dissociation.

Table 2 contains the experimental results and the values of $K_{instab.}$ for beryllium ethylenediaminetetraacetate calculated by means of them.

By using the mean value of this constant for calculating the amount of $Be(OH)_2$ precipitated by ammonia in the presence of excess EDTA-Na taking into account the processes:

$$BeHY^- \rightleftarrows Be^{2+} + HY^{3-} \qquad 1{,}5 \cdot 10^{-9}$$

$$Be^{2+} + 2OH^- \rightleftarrows Be(OH)_2 \qquad 10^{20}\ [11]$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \qquad 1{,}5 \cdot 10^{-5}$$

it is possible to show that precipitation of a 0.1 M solution of a beryllium salt by 1 M ammonia solution in the presence of excess EDTA-Na is 99.7% complete. This, in general, agrees with the observations of many authors who have used this method of precipitation for analytical purposes.

It is interesting to note that if it is assumed that the composition of the complex is represented by BeY^{2-} and the experimental results obtained above are used, the value obtained for $K_{instab.}$ is of the order of 10^{-17}, which cannot explain the fact of the precipitation of $Be(OH)_2$ by ammonia from a solution containing EDTA-Na. A complex with such a constant should be very stable and should not be broken down by ammonia. This fact appears to be a confirmation of the correctness of our assumption that the composition of the beryllium complex is represented by $BeHY^-$.

SUMMARY

On the assumption that the composition of the complex formed between beryllium and EDTA is represented by $BeHY^-$, it has been established by ion exchange on KU-1 cation exchange resin that the instability constant of this complex is $1.5 \pm 0.2 \times 10^{-9}$.

Calculations in which this value of the constant is used give results which are in agreement with experimental data.

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GRAVIMETRIC DETERMINATION OF ZIRCONIUM AFTER ITS PRECIPITATION WITH CYCLOHEXANOL-1-CARBOXYLIC ACID

I. P. Alimarin and Shen Han-Si

M. V. Lomonosov Moscow State University

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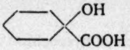
A large number of methods have been developed for the quantitative determination of zirconium using various organic precipitants; the latter include phenylarsonic acid [1], mandelic acid and its derivatives [2-7], phthalic acid [8], tetrachlorophthalic acid [9], fumaric acid [10], and also cupferron [11] and its analog N-benzoylphenylhydroxylamine [12]. In recent years new organic reagents containing the groups SeO_2H, TeO_2H, PO_3H_2 have been suggested for the determination of zirconium, and for its separation from other elements [13, 14]. Among these reagents, mandelic acid and its derivatives have proved to be very interesting since they possess high selectivity. In the work described here we have attempted to use an analog of this acid—cyclohexanol-1-carboxylic acid—as a precipitant for the determination of zirconium and for its separation from accompanying elements:



(cyclohexanol-1-carboxylic acid)

It was established that cyclohexanol-1-carboxylic acid, like mandelic acid, precipitates zirconium from a dilute hydrochloric acid solution while aluminum, iron, beryllium, thorium, uranium, vanadium, tin, titanium, chromium, and the rare earths do not interfere with the determination of zirconium.

EXPERIMENTAL

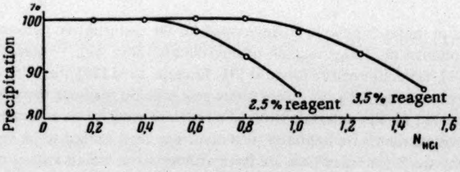
Synthesis of Cyclohexnol-1-carboxylic acid. Cyclohexnol-1-carboxylic acid was synthesized by a modified version of Ultee's method [15]. To 50 g of freshly distilled cyclohexanol was added an excess of a saturated solution of sodium bisulfite. The mixture was stirred until it had crystallized into a thick mass. The bisulfite compound was filtered off, washed with a small amount of water, and a saturated solution of potassium cyanide (25 g) added to the mixture obtained with vigorous stirring. After 20-30 min, when the reaction was complete, the nitrile of cyclohexanol-1-carboxylic acid separated out as an oil. The nitrile was removed to a separating funnel, in which it was heated with four times its amount of concentrated hydrochloric acid on a boiling water bath for 3-5 hours. The white crystalline material which separated out after cooling was the amide of cyclohexanol-1-carboxylic acid. The amide was next heated on a water bath with a small excess of a 10% sodium hydroxide solution for two hours until ammonia had ceased to be liberated. After cooling, the solution was acidified with hydrochloric acid and white crystalline cyclohexanol-1-carboxylic acid separated out. A fairly pure material can be obtained by recrystallizing the product from water. The melting point was 107° (in good agreement with published results). The solubility of the acid in water is 7.3 g/100 ml H_2O (20°). The compound is stable on standing in air; no decomposition was observed over a period of several months.

TABLE 1

Determination of Zirconium in Solutions of its Salts

Zr, g		Error		Zr, g		Error	
taken	found	g	%	taken	found	g	%
0,0024	0,0024	±0,0000	±0,0	0,0119	0,0118	−0,0001	−0,8
0,0024	0,0024	±0,0000	±0,0	0,0357	0,0358	+0,0001	+0,3
0,0119	0,0119	±0,0000	±0,0	0,0357	0,0356	−0,0001	−0,3

Optimum Conditions for Precipitating Zirconium. In order to establish the optimum precipitating conditions, a study was made of the effect of acid and reagent concentrations on the completeness of precipitation of zirconium. For this purpose, various amounts of hydrochloric acid were added to a solution containing a known amount of zirconium, the solutions obtained were diluted with water to 25 ml, and 25 ml of a 5% solution (or 7% solution) of the reagent added; the final solution was heated to the boil. After the solution was cooled, the precipitate was filtered off and washed with 0.1 N hydrochloric acid containing 0.5% of the reagent. The precipitate was dried, calcined to constant weight at 1000°, and weighed as zirconium dioxide. The effect of acid and reagent concentrations on completeness of precipitation is shown in the diagram. The optimum conditions were found to be as follows: the hydrochloric acid concentration should not exceed 0.4 N when 2.5% reagent solution is used; or more than 0.8 N when 3.5 % reagent solution is used. Precipitation can also be carried out in the presence of nitric or perchloric acid of the same normality. In the presence of sulfuric acid, however, as a result of the formation of stable $[ZrO(SO_4)_2]^{2-}$ ions, precipitation is incomplete. Tartrate and citrate ions, and other organic acids which give stable complex ions with zirconium, also interfere with complete precipitation of zirconium.



Effect of HCl concentration and reagent concentration on completeness of zirconium precipitation.

As the values given in Table 1 show, results for the determination of zirconium in solutions of its salts are reasonably accurate and exhibit good reproducibility.

The composition of the precipitates which separate out from solutions with different hydrochloric acid concentrations is variable. Zirconium ions are known to hydrolyze strongly and to polymerize even in acid solution. The ratio of metal to organic addendum in the precipitate separated from 0.5 N hydrochloric acid approximates to 1 : 1.7. The ratio of the metal to the addendum in the precipitate separated from 2 N hydrochloric acid approximates to 1 : 2, which corresponds to a formula of $ZrO(C_7H_{11}O_3)_2$ or $Zr(OH)_2(C_7H_{11}O_3)_2$.

Because the composition of the precipitate varies, the precipitate cannot be weighed after drying; it must be calcined to ZrO_2.

TABLE 2

Determination of Zirconium in the Presence of Foreign Ions

Zr, g		Foreign ions, g		Error	
taken	found			g	%
0,0119	0,0119	Al	0,012	±0,0000	±0,0
0,0119	0,0120		0,060	+0,0001	+0,8
0,0024	0,0024		0,024	±0,0000	±0,0
0,0119	0,0119	Be	0,027	±0,0000	±0,0
0,0119	0,0120		0,133	+0,0001	+0,8
0,0024	0,0025		0,133	+0,0001	+4,0
0,0119	0,0119	Fe$^{(III)}$	0,014	±0,0000	±0,0
0,0119	0,0120		0,143	+0,0001	+0,8
0,0024	0,0024		0,029	±0,0000	±0,0
0,0119	0,0120	Ti	0,017	+0,0001	+0,8
0,0119	0,0120		0,035	+0,0001	+0,8
0,0048	0,0048		0,035	±0,0000	±0,0
0,0119	0,0119	Sn$^{(IV)}$	0,018	±0,0000	±0,0
0,0119	0,0119		0,045	±0,0000	±0,0
0,0024	0,0025		0,045	+0,0001	+4,0
0,0119	0,0118	Th	0,011	—0,0001	—0,8
0,0119	0,0119		0,060	±0,0000	±0,0
0,0024	0,0023		0,060	—0,0001	—4,0
0,0119	0,0118	Total rare earths	0,011	—0,0001	—0,8
0,0119	0,0118		0,072	—0,0001	—0,8
0,0024	0,0024		0,072	±0,0000	±0,0
0,0119	0,0118	U$^{(VI)}$	0,012	—0,0001	—0,8
0,0119	0,0120		0,036	+0,0001	+0,8
0,0024	0,0025		0,050	+0,0001	+4,0

TABLE 3

Determination of Zirconium in Zirconium Bronze

Zr found, %	
mandelic acid method	suggested method
12,95; 13,10; 13,08	12,85; 13,05; 12,90

TABLE 4

Determination of Zirconium in Zircon

ZrO_2 found, %		
phenylarsonate method	mandelic acid method	suggested method
63.8	63.8	63.6
64.0	63.9	63.7

Determination of Zirconium in the Presence of Other Elements in an Alloy and in a Mineral. Zirconium can be readily separated from a number of elements such as aluminum, iron, beryllium, titanium, quadrivalent tin, thorium, sexivalent uranium, and the rare earths (Table 2). Hafnium is coprecipitated with zirconium.

The reagent is no less selective than mandelic acid. Considerably less of it is required for precipitating zirconium.

In order to determine zirconium in zirconium bronze, an aliquot of the latter is dissolved in nitric acid or in a mixture of the latter with hydrochloric acid. After the alloy has dissolved completely, the solution is carefully evaporated almost to dryness, a known amount of hydrochloric acid is then added and the solution diluted to 30 ml with water; 30 ml of a 5% solution of the reagent is added on heating; the precipitate is filtered off, washed, and then calcined to ZrO_2. The method gives satisfactory results.

For the analysis of zircon, 4 g of NaOH is fused in a nickel crucible until sputtering ceases. To the cooled melt a finely ground aliquot of zircon is added and the mixture fused at a dark-red heat until effervesence ceases. Heating is then stopped and 1 g of sodium peroxide added; fusion is continued until oxygen ceases to be evolved (approximately 30-40 min). Zirconium hydroxide is formed on treating the melt with water. The precipitate is filtered off and the filter plus precipitate placed in the beaker in which the melt was decomposed with water; 20 ml of concentrated hydrochloric acid is added, and the beaker heated on a hot plate until the hydroxide has dissolved; 20 ml of water is then added and the liquid filtered. The hydrochloric acid solution is transferred to a 100 ml standard flask, the filter is washed several times with water and the solution made up to the mark with water. The zirconium is determined by taking an aliquot of this solution and precipitating it by the method described above. Results for the determination of zirconium in zircon are given in Table 4.

SUMMARY

A new gravimetric method has been developed for the determination of zirconium, in which cyclohexanol-1-carboxylic acid is used as the precipitant. The precipitate formed has a variable composition. It is therefore calcined to ZrO_2.

It is possible, by means of this method, to determine zirconium in the presence of aluminum, ferric iron, beryllium, quadrivalent tin, titanium, thorium, sexivalent uranium, and the rare earths.

Satisfactory results were obtained when this method was used to determine zirconium in zirconium bronze and zircon.

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A STUDY OF THE COPRECIPITATION OF GERMANIUM WITH THE HYDROXIDES OF IRON AND OTHER METALS

Kh. Ya. Kuus

Tartu State University

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In recent years germanium has been separated by coprecipitation with ferric hydroxide [1-3]. We have carried out a more detailed study of this process using the radiochemically pure isotope of germanium Ge^{71}. In the course of this work the possibility of using coprecipitation of germanium in analytical practice was established in greater detail. At the same time the results obtained make it possible to come to some conclusions regarding the mechanism of the coprecipitation itself.

Radiometric measurments were made on a type B setup with a MST-17 torsion counter. The results were calculated on the basis of the difference between the radioactivities of the solutions before and after carrying out the operations, and also by comparing the activity of the solutions obtained with the activity of a reference solution. Absorption of radiation by the layer of the solution, and changes in volume were taken into account.

TABLE 1

Amount of Ge precipitated with $Fe(OH)_3$ from solution, %	Amount of Ge extracted from the $Fe(OH)_3$ precipitate by Na_2S solution, %
99	97
100	97
100	90
99	89

During a study of the progress of germanium coprecipitation as a function of the completeness of precipitation of ferric hydroxide, we had already shown that complete coprecipitation is tied up with the precipitation of all the iron. Germanium can be quantitatively extracted from solutions in which the germanium concentration is 2-10 μg/ml, when the ratio Fe : Ge is equal to or greater than 25. In contrast to opinions advanced earlier [1], it was established that the presence of a small excess of NH_4OH during the precipitation of ferric hydroxide is more likely to facilitate than hinder quantitative extraction of germanium.

It was also shown that complete extraction of germanium can be achieved by mixing ferric hydroxide precipitate, prepared beforehand, with the germanium solution; it was shown that extraction of germanium during this process differs somewhat from the case where germanium is coprecipitated with the ferric hydroxide as it is formed [4].

Stability with which Germanium is held by the Precipitate. The ferric hydroxide precipitate containing the coprecipitated germanium was treated with carbonic acid solution, ammonium carbonate, and hydrogen sulfide or sodium sulfide solutions. Carbonic acid and ammonium carbonate solutions hardly extracted any germanium; the hydrogen sulfide solution extracted the germanium very incompletely; germanium was readily and quantitatively extracted from the precipitate by sodium sulfide solution.

The experiments were carried out as follows. Germanium was coprecipitated from a solution containing 320 μg germanium with ferric hydroxide (25 mg Fe). The filtered hydroxide precipitate was washed three times

TABLE 2

Ge extracted with $Fe(OH)_3$ from solution, %	Ge extracted from the precipitate, %			Total germanium extracted from the precipitate, %
	wash liquor			
	I	II	III	
99	82	14	3	99
99	82	12	2	96
100	82	13	2	97
100	82	18	3	103

TABLE 3

(Amount of Ge 121 μg)

Salt present	Salt concentration, M	Amount		Ge extracted, %
		Iron, mg	NH_4OH, equivalents per equivalent of iron	
$NaNO_3$	3,8	5	5	100
NH_4NO_3	3,8	5	5	99
$Ca(NO_3)_2$	3,5	20	1,2	96
$NaCl$	3,8	5	5	99
NH_4Cl	3,5	20	1,2	97
$CaCl_2$	3,5	20	1,2	96

with water and then ten times with 5 ml 10% Na_2S solution. Since, as a result of partial peptization of the precipitate, some of the iron passes through the filter, the wash liquor was filtered a second time after standing for a period, and the filter washed once with 5 ml of fresh Na_2S solution. The results obtained are given in Table 1.

Taking into account the possibility of poor contact between the precipitate on the filter and the wash liquors, the experiments were repeated using another variant. The ferric hydroxide plus the coprecipitated germanium were separated by centrifuging rather than by filtration; the precipitate was then washed twice with water and three times with 5 ml of a hot 10% Na_2S solution, the precipitate being carefully mixed with the wash liquors each time. The wash liquors were collected separately and made up to 50 ml with water. The results obtained are given in Table 2.

These experiments confirmed that germanium is held sufficiently strongly by the ferric hydroxide. The fact that germanium can be washed out of the precipitate by means of Na_2S solution could find practical application for concentrating germanium and for purifying it from interfering impurities prior to its analytical determination.

Effect of Foreign Salts. A study was made of the extent to which germanium is coprecipitated with ferric hydroxide, in the presence of considerable concentrations of sodium, calcium, and ammonium nitrates, and sodium, ammonium, and calcium chlorides. The concentrations of the foreign salts varied within the limits 3.8-3.5 M. The results obtained are given in Table 3.

No significant decrease in the extent to which germanium is coprecipitated was observed in the presence of these salts. The small drop in completeness of coprecipitation in the presence of $Ca(NO_3)_2$, NH_4Cl and $CaCl_2$ can be explained on the grounds that at high concentrations of these salts, it is difficult to ensure quantitative precipitation of ferric hydroxide; a larger amount of iron was therefore taken for these experiments. It was also demonstrated that even high concentrations of NH_4OH (up to 15% calculated as NH_3) have no appreciable effect on the extent to which germanium is coprecipitated.

TABLE 4

Partial precipitation of Fe with NH_4OH		Partial dissolution of $Fe(OH)_3$ with H_2SO_4	
amount of NH_4OH expressed as equivalents per equivalent of Fe	Ge coprecipitated, %	amount of H_2SO_4 expressed as equivalents per equivalent of Fe	G coprecipitated, %
0,2	13	0,8	22
0,4	19	0,6	23
0,6	33	0,4	38
0,8	49	0,2	58
1,0	98		

TABLE 5

NH_4OH added, equivalents per equivalent of iron	Germanium extracted, %		
	with fresh precipitate	with precipitate which has stood for 2 hr on a water bath	with precipitate which has stood for 10 hr on a water bath
0,2	0	13	5
0,4	0	12	8
0,6	0	6	10
0,8	10	12	9
0,9	64	37	13
1,0	99	99	100

These experiments confirm that it is possible to extract germanium with ferric hydroxide in the presence of large amounts of foreign salts; this is very important from an analytical viewpoint. They also indirectly indicate that coprecipitation of germanium is not a simple adsorption process.

The next series of experiments were designed to explain the mechanism of the coprecipitation process.

Reversibility of the Coprecipitation Process. In one series of experiments, iron was precipitated from 50 ml of solution containing 125 μg germanium and 25 mg iron by various amounts of NH_4OH; the latter was added in amounts of 0.2, 0.4, 0.6, 0.8, and 1.0 equivalents with respect to iron. In another series the iron was precipitated by an exactly equivalent amount of NH_4OH, and H_2SO_4 solution was then added in amounts of 0.8, 0.6, 0.4, and 0.2 equivalents with respect to one equivalent of iron. The amount of coprecipitated germanium was determined in all the solutions after removal of the precipitate. The results obtained are given in Table 4 and in Fig. 1.

It is obvious that precipitation of germanium with ferric hydroxide is a fully reversible process. The small difference between the curves obtained during partial precipitation of iron (Curve 1), and partial dissolution of the hydroxide precipitate (Curve 2), does not exceed the experimental error, and is the result, presumably, of the fact that equilibrium is not completely established between the solution and the precipitate after addition of acid.

Effect of Precipitate Aging. The effect of aging of the hydroxide precipitate and the effect of basic iron salts on the coprecipitation curve was studied in three series of experiments. NH_4OH in amounts of 0.2, 0.4, 0.6, 0.8, and 1.0 equivalents with respect to iron were added to solutions containing 50 mg iron. The solutions were then allowed to stand in contact with the precipitates for 97 hours. In the first series the solution were kept for two hours out of the 97 on a boiling water bath, while in the second series they were kept for ten hours on a boiling water bath, and in the third series—the control series—the experiments were carried out with fresh precipitates.

After aging of the precipitates, the solutions were made up to 50 ml with water and added to 2 ml of solution containing 420 μg germanium. The precipitates were filtered after 15-20 min.

TABLE 6

NaOH added, equivalents per equivalent of metal	Germanium extracted, %		
	with Mg (OH)$_2$	with Mn (OH)$_2$	with Cu (OH)$_2$
0,2	98	98	7
0,4	99	98	15
0,6	100	97	95
0,8	98	99	89
0,9	99	99	—
1,0	99	98	85

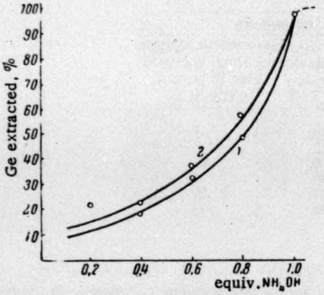

Fig. 1. Reversibility of coprecipitation of Ge. 1) Coprecipitation of Ge during partial precipitation; 2) coprecipitation of Ge during partial dissolution of the precipitate.

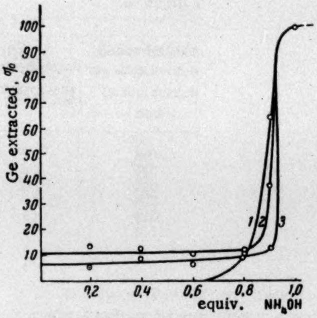

Fig. 2. Effect of precipitate aging on coprecipitation of Ge. 1) Fresh precipitate; 2) precipitate which has stood for 2 hr on a water bath; 3) precipitate which has stood for 10 hr on a water bath.

After filtration, the percentage germanium extracted from the solution was determined. The results obtained are given in Table 5 and in Fig. 2.

It is clear from these results that during the aging of the precipitates of the basic salts and hydroxide of iron, the germanium extraction curve approximates more and more to the vertical line near the equivalence point for the precipitation of ferric hydroxide. On the other hand, there is a characteristic "tail" to the germanium extraction curve during aging of the precipitates.

This phenomenon can be explained on the assumption that during aging of the precipitates, the composition of the latter becomes more homogeneous than that of freshly prepared precipitates, which contain basic salts of different compositions and with the hydroxide as an impurity. The pH jump also becomes sharper as a result of the buffering effect of the precipitates.

During aging, as a result of hydrolysis, almost all the iron is precipitated in the form of basic salts, even from solutions to which little NH$_4$OH has been added. The appearance of a "tail" is explained by simple adsorption of the germanium by the precipitate of basic iron salts which has a fairly significant volume. The precipitates of the basic salts which are obtained immediately after addition of 0.2, 0.4, and 0.6 equivalents of alkali have such a small volume, that adsorption of germanium could not be detected by the technique used.

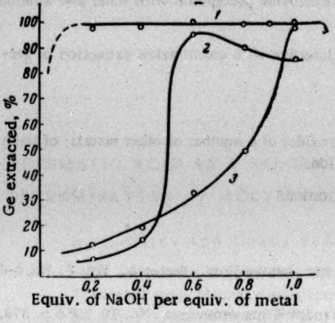

Fig. 3. Coprecipitation curves of Ge with various metals. 1) With Mg(OH)$_2$ and Mn(OH)$_2$; 2) with Cu(OH)$_2$; 3) with Fe(OH)$_3$.

Coprecipitation of Germanium with Magnesium, Manganese, and Copper Hydroxides. In order to study the coprecipitation of germanium with the hydroxides of other metals as a function of the completeness of the precipitation of these hydroxides, we chose magnesium hydroxide (precipitation pH equal to, or about 11), manganese hydroxide (precipitation pH equal to, or about 9), and copper hydroxide (precipitation pH equal to, or about 5). The germanium concentration in the first two series of experiments was 180 μg in 50 ml, while in the experiments with Cu(OH)$_2$ it was 360 μg in 50 ml. The concentration of the metal in all the series was 25 mg in 50 ml. The hydroxides were precipitated with 0.2, 0.4, 0.6, 0.8, 0.9, and 1.0 equivalents of NaOH solution per equivalent of the corresponding metal. The results obtained are given in Table 6 and in Fig. 3.

It is clear that coprecipitation of germanium with the hydroxides of these metals differs essentially from coprecipitation of germanium with ferric hydroxide (Fig. 3). With magnesium and manganese hydroxides, quantitative extraction of germanium is achieved after adding only 0.2 equivalent of NaOH to one equivalent of metal, while with ferric hydroxide germanium is only extracted completely after adding all the requisite amount of alkali. Cupric hydroxide occupies an intermediate position between these extremes; in this case germanium is completely extracted on addition of about 60-70% of the equivalent amount. In our experiments with cupric hydroxide, the small decrease in completeness of germanium coprecipitation towards the end of precipitation of all the copper can be explained by partial dehydration of the hydroxide precipitate, which was observed during removal of the precipitate. It was established that germanium is also quantitatively coprecipitated with Al, Sn, Pb, Ti, and Bi hydroxides.

DISCUSSION OF RESULTS

Coprecipitation of germanium with ferric hydroxide is of very great importance for the extraction of small amounts of germanium from dilute solutions. Combined with subsequent distillation or extraction, this technique enables germanium to be freed from most of the impurities which interfere with its analytical determination. Magnesium and manganese hydroxides could also be used – less successfully – instead of ferric hydroxide.

As for the coprecipitation mechanism, the simplest explanation would be to assume formation of sparingly soluble metagermanates which are then entrained by the precipitate. The absence of coprecipitation during the beginning of the precipitation of Fe(OH)$_3$ and Cu(OH)$_3$ cannot, however, be explained on the basis of this assumption; it is known that ions of metagermanic acid predominate in solution at even lower pH values than those at which the hydroxides indicated are precipitated. It is also difficult to explain the insignificant coprecipitation of germanium with MgNH$_4$PO$_4$ which we established. In addition, it must be assumed that the low solubility of metagermanates is not a probable factor.

It is clear from the experimental results obtained that germanium is coprecipitated with the hydroxides of very many metals, but that quantitative coprecipitation only occurs at pH values which are higher than a certain limit (about six). For solving the question of the mechanism of coprecipitation, which, of course, requires further special investigation it is evident that in order to explain this mechanism it is necessary to look into: 1) The general structural characteristics of sparingly soluble hydroxides, and 2) general changes in the anionic forms of germanium in solution.

We should like to thank A. V. Moskvin for his valuable advice.

SUMMARY

Coprecipitation of germanium with ferric hydroxide is a valuable technique in analytical practice for the quantitative extraction of germanium from dilute solutions.

It is very difficult to wash out the germanium from the ferric hydroxide precipitate with water and ammonia, but quantitative extraction is possible with sodium sulfide solution.

High concentrations of common chlorides and nitrates do not interfere with quantitative extraction of germanium.

The coprecipitation process is reversible.

Germanium is also quantitatively coprecipitated with the hydroxides of a number of other metals; of these magnesium and manganese hydroxides could find practical application.

Some data have been obtained on the mechanism of coprecipitation.

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THIOMALIC ACID AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF MOLYBDENUM

A. I. Busev and Chang Fan

M. V. Lomonosov Moscow State University

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There are published references [1, 2] to the fact that during the interaction of thiomalic acid (mercaptosuccinic) acid HOOC · CH$_2$ · CHSH x COOH with molybdate in a weakly acid (pH about 4.5), or acid (0.3 N H_2SO_4) medium, a yellow colored compound is formed. The sensitivity with which sexivalent molybdenum can be detected when this reaction is carried out in a test tube or by a spot technique is fairly high [1]. Sexivalent tungsten does not give a color [2]. The ions of a number of other elements form soluble colored compounds or precipitates under various conditions [1, 2]. Thiomalic acid has been suggested as a reagent for detecting palladium [3].

Among the aims of the work described here was a study of the reaction between sexi- and quinquevalent molybdenum and thiomalic acid, and establishment of the possibility of carrying out a quantitative photometric determination of molybdenum by means of this reagent. The interaction of molybdenum with thioglycolic acid has been studied in the same way [4].

EXPERIMENTAL

Thiomalic acid was synthesized by interaction of maleic acid with excess sodium hydrosulfide [5]. After three recrystallizations from diethyl ether, the thiomalic acid prepared had a melting point of 146-147° (published figure, 149-150°). The SH content of the product obtained, as determined by the method of Obtemperenskaya, Terent'ev, and Buzlanova* [6], was 21.92, 22.19, and 22.08% (theoretical value 22.05% SH). It should be pointed out that the reagent used for the photometric determination of molybdenum need not be subjected to such careful purification.

Thiomalic acid is a white crystalline material which is readily soluble in water. It is completely stable in air, does not possess a disagreeable odor, has reducing properties, and is readily oxidized by iodine solution

Solutions of thiomalic acid were prepared by dissolving accurately weighed aliquots of the carefully purified preparation in water. Their concentrations were determined by titration with alkali solution using a glass electorde (the acid is dibasic), and iodometrically [7]; the latter method is based on oxidation of thiomalic acid with excess iodine solution in a strongly alkaline medium, followed by back titration of the iodine with thiosulfate solution, after acidification. All the remaining solutions and apparatus used were the same as those described previously.

Valence of Molybdenum in its Compounds with Thiomalic Acid. Under certain conditions, thiomalic acid forms colored compounds with molybdenum in its quinque- and sexivalent states.

Trivalent molybdenum (in the form of weak hydrochloric acid solutions of $(NH_4)_2MoCl_5$) does not give characteristically colored compounds with thiomalic acid at pH 1-4.

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* The determinations were carried out by M. M. Buzlanova whom the authors wish to thank.

Quinquevalent molybdenum as $(NH_4)_2MoOCl_5$, at acidities varying from 0.5 M HCl to pH 7, interacts with thiomalic acid, a yellow color being formed. At pH > 7 the color intensity decreases, and at pH > 9 the solution becomes colorless. When such a solution is acidified to pH 3-5 a yellow color reappears. Excess thiomalic acid prevents hydrolysis of quinquevalent molybdenum when the pH is increased; the solution remains colorless.

Sexivalent molybdenum reacts with thiomalic acid at pH 2-5. A greenish-yellow color appears almost instantaneously, and it is stable in air when excess thiomalic acid is present. The valence of molybdenum at pH 3-6 does not change in the presence of excess thiomalic acid (see below), although the latter possesses clearly evident reducing properties. On adding the minimum amount of thiomalic acid to 0.1 M molybdate solution (pH 4) a yellow color is formed which is unstable, and after 5-10 min changes into the blue (molybdenum blue is formed).

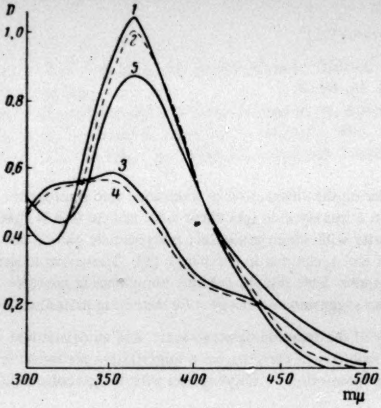

Fig. 1. Absorption curves for solution of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid at various pH's. 1) Sexivalent molybdenum compound at pH 3.52; 2) sexivalent molybdenum compound obtained by mixing solutions of $(NH_4)_2MoOCl_5$ and thiomalic acid at pH > 10, after standing for several minutes (oxidation of Mo^V to Mo^{VI}) the pH was then adjusted to 4.58; 3) quinquevalent molybdenum compound at pH 1.48; 4) sexivalent molybdenum compound obtained by mixing solutions of molybdate and thiomalic acid and adjusting the pH to 0.68; 5) quinquevalent molybdenum compound at pH 5.52. In all cases [Mo] = 2.0×10^{-4} M; [RSH] = 0.02 M; l = 1 cm. The optical density was measured relative to water.

Photometric Characteristics of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid. Absorption curves for solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid (Fig. 1) were obtained as follows: To 2.5 ml of a 2×10^{-3} M sodium molybdate solution or a solution of a salt of quinquevalent molybdenum in 1 M HCl, contained in a 25 ml standard flask, was added 10 ml of water and 5 ml of 0.1 M thiomalic acid with a pH of 4-5; the acidity of the solution was adjusted to a definite value by careful dropwise addition of sodium hydroxide or hydrochloric acid solutions with efficient stirring. During this process it is necessary to avoid local increases in acid or alkali concentration. When more than the requisite amount of acid (or alkali) was added, the solution was discarded. Only by observing these precautions is it possible to avoid premature partial reduction of sexivalent molybdenum at low pH values, and oxidation of quinquevalent molybdenum at high pH values. Afterwards the solution was diluted to the mark and the pH measured with a glass electrode. A solution of the compound of quinquevalent molybdenum with thiomalic acid with a pH of 5.52 was obtained by adding an acetate buffer solution with a pH of 7. Since thiomalic acid solutions do not absorb light in the 300-700 mμ region, the optical density was measured with respect to water on a SF-4 spectrophotometer in a cuvette with a layer thickness of 1 cm*.

The absorption curve of solutions of the compound of sexivalent molybdenum with thiomalic acid at pH 3.52 has a maximum at 365 mμ (Fig. 1, Curve 1). The absorption curve of solutions of the compound of quinquevalent molybdenum with thiomalic acid at pH 1.48 has a maximum at 352.5 mμ. The absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with thiomalic acid are similar to the absorption curves of the corresponding compounds of molybdenum with thioglycolic acid for solutions with the same pH values [4].

During determination of the molar extinction coefficients of solutions of the compounds of sexivalent and quinquevalent molybdenum with thiomalic acid at various pH's, the optical density was measured at 365 mμ

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* The disulfide, as well as molybdate, hardly absorbs any light in the 300-700 mμ region.

TABLE 1

Molar Extinction Coefficients of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid (Concentrations, 2.0×10^{-4} M Mo^{VI} or Mo^{V} and 0.02 M thiomalic acid; layer thickness 1 cm)

Mo valence	D^{365}	ε^{365}_{M}	Acidity
Mo^{VI}	1,05	5250	pH 4,47
	1,05	5250	pH 4,04
	0,532 *	2660	0,3 *N* HCl
	0,523 *	2610	0,6 *N* HCl
Mo^{V}	0,510	2550	pH 1,26
	0,538	2690	pH 1,48
	0,518	2590	pH 1,55
	0,890	4450	pH 5,52
	0,950	4250	pH 5,50

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* The final thiomalic acid concentration was 0.06 M; the optical density was measured 20 min after preparing the solution. At this acidity sexivalent molybdenum is reduced to the quinquevalent state.

in the presence of a large excess of thiomalic acid. The molar extinction coefficients (Table 1) were calculated with respect to the molar concentration of molybdenum.

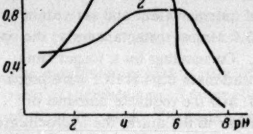


Fig. 2. Effect of pH on the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid. [Mo] = $= 2.0 \cdot 10^{-4}$; [RSH] = 0.02 M. 1) Solution with sexivalent molybdenum- 2) solution with quinquevalent molybdenum.

Acidity Limits Within Which the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid Exist. The solutions used for establishing the acidity limits within which the compounds of sexi- and quinquevalent molybdenum with thiomalic acid exist were 2×10^{-4} M relative to sodium molybdate or to a salt of quinquevalent molybdenum in 1 N HCl, and 0.02 M relative to thiomalic acid. The pH of the solution was adjusted to the requisite value very carefully. In the case of quinquevalent molybdenum the pH of the solution was adjusted by addition of an acetate buffer solution with varying pH values, with careful stirring; the pH was finally measured with a glass electrode. The optical density was measured at 365 mμ relative to water, one hour after the pH had been determined (when the optical density had become constant).

The thiomalate of sexivalent molybdenum exists within the pH range 2 to 6; the optimum optical density is observed at pH 3-5 (Fig. 2). On increasing the pH from 6 to 8, the intensity of the greenish-yellow color rapidly decreases. There is a decrease in optical density below pH 3 also, presumably as a result of the reduction of sexivalent molybdenum with thiomalic acid, and the formation of the compound of quinquevalent molybdenum with thiomalic acid which has a relatively less intense yellow color.

Absorption curves for solutions of a mixture of sexivalent molybdenum and a large excess of thiomalic acid at pH 0.68, after standing for a long time, and for solutions of a mixture of a quinquevalent molybdenum salt with thiomalic acid at pH 1.48, almost coincide (Fig. 1, Curves 4 and 3; the molar molybdenum concentration in both cases was the same). This shows that at pH 0.68, sexivalent molybdenum is reduced to the quinquevalent state by thiomalic acid, and forms a yellow colored compound with excess of the latter. This conclusion is also confirmed by the coincidence observed between the calculated molar extinction coefficients of solutions obtained by mixing a salt of sexivalent molybdenum with thiomalic acid at a concentration of 0.3-0.6 N HCl, and of solutions of the compound of quinquevalent molybdenum and thiomalic acid at pH 1.48 (Table 1.).

The compound of quinquevalent molybdenum with thiomalic acid is stable at acidities ranging from 0.3 M to pH 7.5. The maximum optical density is observed at pH 4.5-6.5. On increasing the pH to 10 upwards, the solutions of the compound of quinquevalent molybdenum with thiomalic acid remain clear in the presence of excess of the latter. When the solution thereby obtained is carefully acidified with hydrochloric acid to a pH of 3-5, a greenish-yellow color appears (in contrast to the yellow color of the quinquevalent molybdenum compound at this same pH), the molar extinction coefficient being 5050. The absorption curve of the compound of sexivalent molybdenum with thiomalic acid at the same molar concentration (Curve 1, Fig. 1); these results show that quinquevalent molybdenum is oxidized to the sexivalent state by atmospheric oxygen or by water ions in the alkaline medium, even in the presence of excess thiomalic acid.

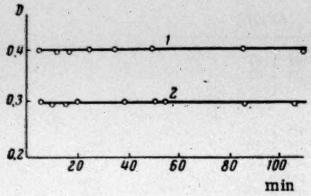
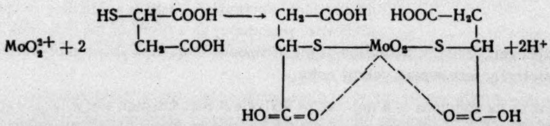


Fig. 3. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid, and time. The concentration of the sexi- and quinquevalent molybdenum was the same and equal to 8×10^{-5} M; thiomalic acid concentration 8×10^{-3} M; pH 3.6. 1) Compound of sexivalent molybdenum; 2) quinquevalent molybdenum compound.

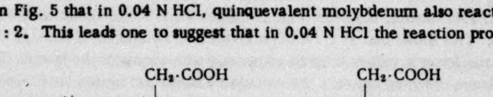
The compounds of molybdenum in the sexi- and quinquevalent state are almost stable with time at pH 3.6 in the presence of excess thiomalic acid (Fig. 3); reduction of sexivalent or oxidation of quinquevalent molybdenum does not occur.

The Composition of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid. The molar ratios in which sexi- and quinquevalent molybdenum interact with thiomalic acid were established by the isomolar series methods. Different volumes of a 0.02 M solution of sodium molybdate or of a quinquevalent molybdenum salt (in 1 N HCl) were mixed with an almost neutral 0.02 M solution of thiomalic acid, so that the sum of the molar concentrations of both components in the final solution (after dilution) was always 9.6×10^{-4} M. The acidity of the solutions was adjusted by addition of 5 ml of an acetate buffer with pH 3.6 (in the case of sexivalent molybdenum) or by the calculated amount of hydrochloric acid until its concentration was 0.04 N HCl (in the case of quinquevalent and sexivalent molybdenum). Sexivalent molybdenum interacts with thiomalic acid at pH 3.6 almost instantaneously; the optical density was measured not later than 20 min after preparing the solutions. On standing for a longer time, some of the solutions containing excess sexivalent molybdenum turned blue. Solutions in 0.04 N HCl were prepared as follows: after mixing the solutions of the molybdenum salt, thiomalic acid, and the requisite amounts of hydrochloric acid, the final solution obtained was immediately diluted with water to the mark; the hydrochloric acid concentration was 0.04 N (taking into account the hydrochloric acid in the original solution). In order to attain equilibrium, in the case of sexivalent molybdenum, the solutions were allowed to stand for three hours, while in the case of quinquevalent molybdenum they were allowed to stand one hour. The optical density of solutions of the compound of quinquevalent molybdenum with thiomalic acid was measured relative to solutions of a quinquevalent molybdenum salt of equal molar concentration and of the same pH, but not containing thiomalic acid.

It is clear from Fig. 4 that the maximum optical density of solutions at pH 3.6 is observed at a molar ratio of sexivalent molybdenum to thiomalic acid of 1 : 2. The reaction probably proceeds as follows:



It is clear from Fig. 5 that in 0.04 N HCl, quinquevalent molybdenum also reacts with thiomalic acid in the molar ratio of 1 : 2. This leads one to suggest that in 0.04 N HCl the reaction proceeds according to the following equation:



$$Mo_2O_3^{4+} + 4\begin{array}{l} CH_2\cdot COOH \\ \;| \\ HS-CH\cdot COOH \end{array} \longrightarrow Mo_2O_3(S-\overset{\overset{CH_2\cdot COOH}{|}}{C}H\cdot COOH)_4 \;\; + 4H^+ \ldots$$

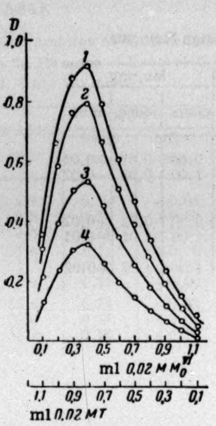


Fig. 4. Interaction of sexivalent molybdenum and thiomalic acid at pH 3.6; the optical density was measured relative to water. 1) At 360 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

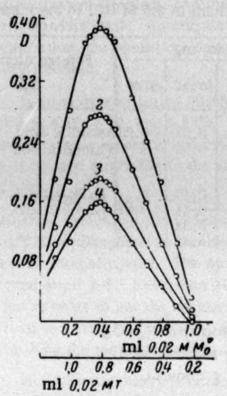


Fig. 5. Interaction of quinquevalent molybdenum and thiomalic acid in 0.04 N HCl; the optical density was measured relative to solutions of a quinquevalent molybdenum salt with equal molar concentration in 0.04 N HCl. 1) At 350 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

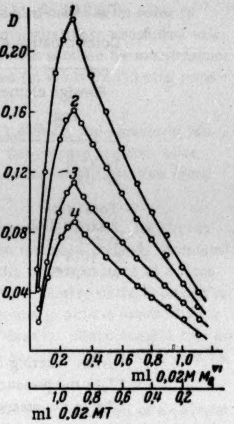


Fig. 6. Interaction of sexivalent molybdenum with thiomalic acid in 0.04 N HCl; the optical density was measured relative to water. 1) at 350 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

The maximum optical density in experiments with sexivalent molybdenum in 0.04 N HCl is found at a molar ratio of molybdenum to thiomalic acid of 1 : 3 (Fig. 6), i. e., one mole of molybdate corresponds to three moles of thiomalic acid. The results obtained show that during the interaction of sexivalent molybdenum in 0.04 N HCl, one mole of thiomalic acid is used up in reducing the molybdate to the quinquevalent state; subsequently two moles of thiomalic acid react with one mole of quinquevalent molybdenum. Similar results were obtained during a study of the interaction of sexi- and quinquevalent molybdenum with thioglycolic acid [4].

Experiments on electrophoresis showed that the yellow colored compound of sexivalent molybdenum at pH 5.1, and that of quinquevalent molybdenum in 0.2 N HCl move toward the anode, i. e., thiomalic acid forms colored anionic complexes with molybdenum.

Photometric Determination of Mo with Thiomalic Acid in a 0.5 N Hydrochloric Acid Medium. As shown above, when a large excess of thiomalic acid is present in moderately acid solutions, the former completely reduces sexivalent molybdenum to its quinquevalent state, which then reacts with excess reagent to give a fairly intense yellow color. In 0.3-0.6 N HCl the optimum density is obtained 20 min after preparing the solutions, and thereafter remains constant for at least one day. In order to get the maximum optical density for a solution with a concentration of 2×10^{-4} M molybdate in a medium of 0.5 N HCl, it is necessary to add more than 10 ml of 0.1 M thiomalic acid for a final volume of 25 ml. In 0.3-0.6 N HCl most accompanying elements do not form colored compounds with thiomalic acid.

A calibration curve is obtained as follows. Twelve ml of a standard solution of sodium molybdate containing not more than 1 mg molybdenum is placed in a 25 ml standard flask, and about 2 ml of dilute hydrochloric acid [1 : 1] is added; in this case the HCl concentration in the final solution will be 0.5 N. 7.5 ml of 0.2 M thiomalic acid solution is added and the solution diluted with water to the mark; it is then well mixed, and after 20 min the optical density is measured at 350, 365, 380, 400, or 420 mμ relative to water.

TABLE 2

Determination of Molybdenum in 0.5 M HCl in the Presence of Foreign Elements

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error
Ti 37,3	0,50	0,53	+0,03	Ascorbic acid 500	0,60	0,61	+0,01
Zr 100	0,50	0,50	0	Thiourea 500	1,00	0,98	−0,02
Total rare earths 29.5	0,50	0,50	0	Fe 28,0 ($FeCl_3\,6H_2O$) **	0,30	0,32	+0,02
V 1,7	0,50	0,51	+0,01	Cu 1,3 ($CuSO_4 \cdot 5H_2O$) ***	1,00	1,01	+0,01
Cr 10,4	0,30	0,32	+0,02				
W 10,0 *	0,30	0,32	+0,02	Cu 3,2 ***	1,0	1,02	+0,02

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* After filtering off the turbidity of H_2WO_4.

** In the presence of 0.6 g ascorbic acid.

*** In the presence of 0.5 g thiourea.

TABLE 3

Determination of Molybdenum in the Presence of Foreign Elements at pH 3,6

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error		taken	found	error
Ba 2,75	0,77	0,79	+0,02	Mn 2,20	0,77	0,78	+0,01	Cu 2,79	0,77	0,41	−0,36
Mg 1,21	0,77	0,75	−0,02	Mn 2,75	0,77	0,74	−0,03	Cr 0,26	0,19	0,19	0,00
Ca 0,40	0,77	0,75	−0,02	V 0,26	0,77	0,79	+0,02	Cr 0,52	0,19	0,18	−0,01
Ca 1,60	0,77	0,80	+0,03	V 1,02	0,77	0,78	+0,01	Cr 0,52	0,19	0,18	−0,01
C 1,12	0,77	0,73	−0,04	Be 1,76	0,77	0,77	0,000	Cr 1,04	0,19	0,18	−0,01
Ni 1,17	0,77	0,78	+0,01	Al 1,30	0,77	0,30	−0,37	Cr 1,56	0,19	0,19	0,00
Zn 0,33	0,77	0,75	−0,02	Al 0,20	0,77	0,23	−0,54	Cr 2,60	0,19	0,17	−0,02

The solutions conform to Beer's law at concentrations from 1 to 40 μg Mo/ml.

Molybdenum was determined in synthetic mixtures using the same conditions but with the difference that the solution was neutralized first. The results obtained are given in Table 2. Large amounts of zirconium and titanium do not interfere in 0.5 N HCl. If hydrolysis products separate out during neutralization of the solution, on adding the requisite amount of hydrochloric acid and heating, the precipitate dissolves. Large amounts of trivalent iron do not interfere with the determination, if it is first reduced to the divalent state with ascorbic acid (the molybdate is also reduced to the quinquevalent state during this process). Vanadate is reduced by the reagent to the quadrivalent state, and gives a blue color which does not interfere with the determination. Tungstate does not give a color with the reagent, but in 0.5 N HCl a precipitate or suspension is formed. Separation of tungstic acid strongly affects the optical density, and accordingly it must be filtered off through a filter paper. Copper gives a yellow color with the reagent in 0.5 N HCl and interferes with molybdenum determination. Nevertheless, even large amounts of copper do not interfere when this element is complexed with excess thiourea. Large amounts of chromium and the rare earths do not interfere with molybdenum determination. In 0.5 N HCl a considerably smaller number of elements interfere with the determination of molybdenum than when the determination is carried out at pH 3-5, in 0.5 N HCl, however, the method is less sensitive.

Molybdenum can be determined in steels,or in alloys containing zirconium and titanium,by means of thiomalic acid. To 0.25 g of such an alloy is added 50 ml of HCl 1 : 1 and the mixture heated until complete so-

TABLE 4

Determination of Molybdenum in the Presence of Iron at pH 3.6 (0.77 mg Mo taken)

Fe added, mg	Mo found, mg	Mo error, mg
1,7	0,76	—0,01
2,8	0,77	+0,00
5,6	0,74	—0,03
5,6	0,71	—0,06
5,6	0,80	+0,03
11,2	0,77	+0,00
16,8	0,74	—0,03
22,0	0,78	+0,01
35,5	0,78	+0,01

lution has been effected; nitric acid is then added dropwise in order to oxidize trivalent titanium, and the solution quantitatively transferred to a 100 ml standard flask. An aliquot of this solution is taken for molybdenum determination, the operations described above (in 0.5 N HCl) being subsequently followed.

In an alloy containing 93.45% Ti and 1.47% Zr, the amount of Mo found was 4.38, 4.60, and 4.67%. Using the thiocyanate method, after chromatographic separation of molybdenum, assistant Mu Bin-Ven found 4.69, 4.63, and 4.69% Mo in the same alloy.

Photometric Determination of Molybdenum at pH 3.6. As already established, sexivalent molybdenum forms an intensely colored, completely stable yellow compound in weakly acid media in the presence of a large excess of thiomalic acid. The optimum optical density of the solutions is observed at pH 3-5. More than 10 mg of thiomalic acid is required for 1 mg Mo in order to get the optimum optical density. Since acetate ions do not lead to a drop in the optical density, an acetate buffer can be used for establishing the requisite acidity.

A calibration curve is constructed as follows: to 25 ml of an almost neutral solution of sodium molybdate of known concentration contained in a 50 ml flask, and containing not more than 1.2 mg Mo, is added 5-10 ml of acetate buffer and 3.0 ml of a 0.5% aqueous solution of thiomalic acid. The volume of the liquid is made up to the mark, mixed, and the optical density measured on a spectrophotometer in a cuvette with a layer thickness of 1 cm at 365 mμ relative to water. The solutions conform to Beer's law within the limits 1 to 40 μg Mo/ml.

TABLE 5

Determination of Molybdenum in the Presence of Tungsten (0.77 mg Mo taken)

W, mg	Mo, mg 360 mμ found	error	380 mμ found	error	400 mμ found	error	420 mμ found	error
1,0	0,87	+0,10	0,81	+0,04	0,78	+0,01	0,79	+0,02
5,0	0,86	+0,09	0,80	+0,03	0,75	—0,02	0,76	—0,01
6,0	0,87	+0,10	0,89	+0,03	0,75	—0,02	0,78	+0,01
10,0	0,94	+0,17	0,81	+0,04	0,71	—0,06	0,70	—0,07
10,0	0,94	+0,17	0,83	+0,06	0,74	—0,03	0,74	—0,03
10,0	0,94	+0,17	0,83	+0,06	0,77	+0,01	0,80	+0,03
15,0	0,94	+0,17	0,77	0,00	0,75	—0,02	0,75	—0,02
20,0	0,98	+0,21	0,83	+0,06	0,75	—0,02	0,75	—0,02

Determination of Molybdenum in the Presence of Foreign Elements at pH 3.6. Trivalent iron at pH 1-5 forms a blue colored, soluble compound with thiomalic acid. Nevertheless, the blue color of the solutions rapidly disappears, probably, because of the reduction of trivalent iron to the divalent state. Iron does not interfere with the determination of molybdenum. Tungsten does not give colored compounds with thiomalic acid. In the presence of this element, however, appearance of the colored molybdenum compound is delayed. The higher the tungsten concentration, the slower the rate at which the color develops. When not more than 5 mg of W is present, the optical density reaches its maximum value in half an hour, while in the presence of 5-20 mg of W, it takes 1-2 hours to reach its maximum value. It should be pointed out that the potassium tungstate solution itself absorbs only to a small extent at 300-400 mμ.

TABLE 6

Determination of Molybdenum in Steel

Aliquot No.	Standard sample No.31-V, chromenickelmolybdenum steel* (0.27% Mo)		Standard sample No. 158 steel** (2.23 % Mo)	
	found	error	found	error
1	0,25	−0,02	2,13	−0,10
	0,27	0	2,25	+0,02
	0,28	+0,01	2,21	−0,02
2	0,27	0	2,17	−0,06
	0,30	+0,03	2,34	+0,11

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* Content of other elements (%) Mn$_4$ 0.365; Si 0.275; S 0.017; P 0.023; Cr 1.24; Ni 3.40.

** Content of other elements (%) Mn$_4$ 0.87; Si$_4$ 0.70; S 0.008; P 0.032; Cr 13.18; Ni 12.71; Co 10.35; W 3.03; V 0.03; Nb 1.08.

Accordingly, the optical density must be measured at 400 mμ; in this case, however, the sensitivity of molybdenum determination decreases significantly. Ba, Mg, Ca, Ni, Cd, Zn, Mn, and Be do not interfere with molybdenum determination; vanadium gives a green-blue color with thiomalic acid, this color slowly disappears in the presence of excess reagent. Small amounts of vanadium do not interfere with molybdenum determination. Copper interferes with the determination, since it gives a cherry color with the reagent; aluminum interferes. Small amounts of chromium do not interfere, as long as the test solution is first acidified with hydrochloric acid, a small excess of reagent is added (10 ml of a 0.5% aqueous solution of reagent for 50 ml) and the solution finally neutralized by addition of alkali.

Results for the determination of molybdenum in the presence of foreign ions at pH 3.6 are given in Table 3. Cyanide and acetate anions do not interfere with molybdenum determination. Sodium ethylenediaminetetraacetate, oxalic acid, citric acid, and tartaric acid strongly depress the optical density of the solution and should be absent. Since CN^- ions do not interfere with molybdenum determination, it might be possible to determine molybdenum in the presence of copper after masking the latter with cyanide.

In order to determine molybdenum in the presence of iron, 0.5% aqueous thiomalic acid solution is added dropwise with continuous vigorous stirring to the acid solution (pH 1-2) containing Fe^{III} until the blue color ceases to appear. When large amounts of iron are present, a saturated thiomalic acid solution is added. Toward the end of this operation the reagent should be added slowly, and several seconds allowed to elapse between addition of each drop until the blue color has disappeared completely. A further 5 ml of the reagent is added, followed by alkali solution until a weakly acid or neutral reaction is given (a white turbidity sometimes appears during neutralization, but this disappears toward the end of the neutralization). 5-10 ml of acetate buffer is added (a violet color sometimes appears at this stage, but this disappears after a few minutes), and the volume of the solution made up to the mark, the solution is mixed, and after 15-30 min its optical density is measured relative to water when small amounts of iron are present ($<$ 5 mg). When large amounts of iron are present, measurements are made relative to a solution containing approximately the same amount of iron, and which has been prepared in the same way. Results obtained are given in Table 4.

In order to determine molybdenum in the presence of tungsten, 5-10 ml of acetate buffer solution and 3.0 ml of 0.5% aqueous thiomalic acid solution are added to 25 ml of an almost neutral test solution containing not more than 1.2 mg Mo and not more than 20 mg W. After mixing, the solution is allowed to stand for 1-2 hr; it is then diluted to 50 ml, mixed, and its optical density measured at 400 mμ relative to water. Results for the determination of molybdenum in the presence of tungsten are given in Table 5.

Molybdenum is determined in steel at pH 3.6 by dissolving 1 g of steel in 20 ml HNO_3 (1 : 1) and 20 ml H_2SO_4 (1 : 1) in a 300 ml beaker, and evaporating the solution obtained to the appearance of white fumes.

When the steel does not dissolve completely, 20 ml of HCl (1 : 1) is added, and the solution evaporated to dryness; this operation is repeated several times. After cooling, 80 ml of water is added and the mixture heated until complete solution of the salts is attained. Silicic acid is filtered off on a filter paper, the filter plus residue are washed several times with water and the filtrates collected in a 200 ml flask; after cooling, the volume is made up to the mark with water. A few ml of the solution obtained is pipetted into a 50 ml flask and the solution prepared in the same way as that adopted for construction of the calibration curve; the optical density is measured on a spectrophotometer and the amount of molybdenum determined by means of the calibration curve. Results for the determination of molybdenum in standard samples of alloy steel Nos. 158 and 31-V are given in Table 6.

Thiomalic acid can be used for the photometric determination of molybdenum in the same way as thioglycolic acid. The advantage of thiomalic acid over thioglycolic acid is that the former is easier to handle, and has a lower tendency to be oxidized by atmospheric oxygen.

SUMMARY

The interaction of sexi- and quinquevalent molybdenum with thiomalic acid has been studied under various conditions. It has been shown that the reaction proceeds in a similar way to the reaction with thioglycolic acid.

Two variants have been developed for the photometric determination of small amounts of molybdenum (in a 0.5 N HCl medium and at pH 3.6). The selectivity of the method in a 0.5 N HCl medium is considerably higher than at pH 3.6, but the sensitivity is less.

The methods developed can be used for the determination of molybdenum in multialloyed steels.

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2,7-BIS-(4-CHLORO-2-PHOSPHONOBENZENEAZO)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID (CHLOROPHOSPHONAZO III), A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF URANIUM

A. A. Nemodruk, Yu. P. Novikov, A. M. Lukin, and I. D. Kalinina

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, and The All-Union Scientific-Research Institute of Chemical Reagents, Moscow

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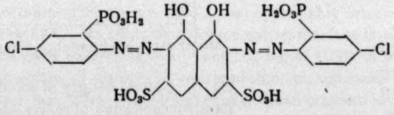
In a previous communication [1] we described a method for the photometric determination of sexivalent uranium by means of 2-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (chlorophosphonazo I) which is the first organic color reagent containing the group PO_3H_2. The introduction of this group into the molecule of an organic reagent enables the reagent to interact with a number of cations in considerably stronger acid solution than is possible in the case of reagents with an analogous structure containing the groups AsO_3H_2, COOH, or OH instead of PO_3H_2. The synthesis and study of other representatives of this class of reagents is undoubtedly of considerable interest. The present article is devoted to the results of an analytical study of a new reagent which is a structural analog of arsenazo III, a reagent recently suggested by Savvin [2]; this new reagent is–2,7-bis-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (chlorophosphonazo III), which we also studied from the point of view of its possible use for the photometric determination of sexivalent uranium.



Chlorophosphonazo III is readily soluble in water. Aqueous solutions at pH < 3 have a rose color. On increasing the pH to 3.0 the rose color acquires a violet tinge, while at pH 4 upwards it changes to violet. Solutions of chlorophosphonazo III in concentrated sulfuric and hydrochloric acids have a bright-green color. In concentrated nitric acid the bright-green color rapidly disappears as a result of oxidation of the reagent. In dilute nitric acid solutions (up to 3 N) chlorophosphonazo III possesses a stable rose color. Chlorophosphonazo III gives a greenish-blue color to solutions of sodium acetate and bicarbonate, a light-blue color to solutions of aluminum hydroxide and the carbonates of the alkali elements, and a blue color to solutions of the caustic alkalis.

Chlorophosphonazo III reacts with the ions of many elements in acid solutions. In the presence of Al^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Tl^{+}, VO^{2+} and the rare earths, the rose color of solutions of the reagent changes to pale blue, while in the presence of Ba^{2+}, Sr^{2+}, Ca^{2+}, Be^{2+}, Ni^{2+} and Pb^{2+} it becomes turquoise. During the reaction with Cr^{III} salts the turquoise color appears gradually, and only develops to its fullest extent after 15-20 min (on heating, this color change from rose to turquoise is completed appreciably more quickly).

The color change with the greatest contrast is observed in the presence of Ce^{IV}, Ti^{IV}, Zr, Hf, Th, U^{VI} and U^{IV}; the color change in these cases is from rose to green. Interaction of chlorophosphonazo III with other elements is not accompanied by an essential change in the color of the solutions of the reagent.

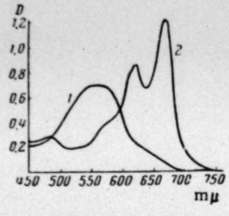


Fig. 1. Optical density of solutions of chlorophosphonazo III and of its compound with sexivalent uranium at pH 1.0. 1) 1.6×10^{-5} M solution of chlorophosphonazo III; 2) solution of the uranium compound containing 1.6×10^{-5} M chlorophosphonazo III and 7.6 mg U/ml. 10 mm cuvette.

It should be pointed out that the color reaction of chlorophosphonazo III with Ce^{IV}, Ti^{IV}, Zr, Hf, Th, U^{VI}, and U^{IV}, apart from its high contrast, possesses a very high sensitivity. The UO_2^{2+} ion is outstanding in this respect; it is the only doubly charged ion which forms a green colored compound with chlorophosphonazo III.

Absorption curves for solutions of chlorophosphonazo III and of its compound with sexivalent uranium are shown in Fig. 1. The maximum absorption of chlorophosphonazo III solutions is observed at 555 mμ, while the maximum absorption of solutions of the uranium compound are observed at 620 mμ and at 670 mμ. The absorption of the reagent in the region of the latter maximum is insignificant.

Compared with other reagents (including arsenazo III), chlorophosphonazo III reacts with sexivalent uranium in more acid solutions. From pH 4 and down to an acidity of about 0.5 N with respect to HCl, the absorption of solutions of the compound remains constant (Fig. 2). The independence of the absorption of the acidity means that uranium can be determined without establishing the pH carefully, and no special buffer solutions have to be used.

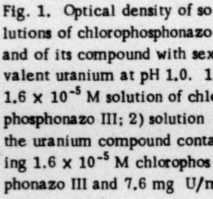


Fig. 2. Optical density of solutions of chlorophosphonazo III and of its compound with sexivalent uranium as a function of the acidity of the solution. 1) 1.6×10^{-5} M chlorophosphonazo III solution, wavelength 555 mμ, cuvette 10 mm; 2) solution of the compound (1.0×10^{-5} M with respect to uranium and 1.6×10^{-5} M with respect to chlorophosphonazo III), wavelength 670 mμ, cuvette 10 mm.

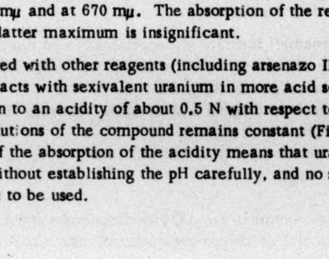


Fig. 3. Optical density of solutions with a constant concentration of sexivalent uranium and variable concentrations of chlorophosphonazo III. The uranium concentration was 0.780×10^{-5} M in all the solutions.

The optical density of the solutions reaches its maximum value immediately after the chlorophosphonazo III solution has been added, and does not change for more than 48 hr.

It was established by the isomolar series method that sexivalent uranium reacts with chlorophosphonazo III in the proportion of 1 : 1. The same

TABLE 1

Molar Extinction Coefficients of Solutions of the Compound of Sexivalent Uranium with Reagents Used for its Photometric Determination

Reagent	Molar extinction coefficient
Ammonium thiocyanate	3031 ± 26 [5]
Quercetin	12.800 [4]
Dibenzoylmethane	17.810*
Arsenazo I	22.800 [3]
1-(2-Pyridylazo)-2-naphthol	23.000 [6]
Chlorophosphonazo I	23.100 [1]
Arsenazo III	75.500*

* Calculated from the curve obtained during the photometric titration of a solution with a constant U^{VI} concentration.

TABLE 2

Interference from Foreign Elements during the Photometric Determination of U^{VI} by Means of Chlorophosphonazo

Interfering element	Permissible weight ratio of interfering element to uranium
Th, Zr, Hf, Ce^{IV}	0,05—0,1
Ti^{IV}	0,15
Bi, rare earths	0,2—0,3
Fe^{III}	0,35
Sn^{IV}	0,5
Pb	1
Cu, Nb, Ta, VO_2^{2+}	2—5
Ca, Sr, Ba, Be, Al	5—10
Fe^{II}	15
Cr^{III}	20
Zn, Ni, Hg^{II},	75—100
Tl^{III}	150
Co, Cd, Mu^{II}, Mg, Sb^{III}	200—250

result was obtained by the method of photometric titration in which the concentration of sexivalent uranium was kept constant and that of the chlorophosphonazo III was varied (Fig. 3). The sharp break on the curves indicates that the compound formed possesses a high stability.

The fact that there was only one break on the curves obtained during photometric titration, both when the concentration of sexivalent uranium was kept constant and that of chlorophosphonazo III was varied, and when the concentration of chlorophosphonazo III was kept constant while that of sexivalent uranium was varied, shows that, apart from the complex in which the ratio of reagent to uranium is equal to 1 : 1, no complexes with other compositions are formed.

The molar extinction coefficient, calculated from the photometric titration curve (Fig. 3), proved to be 78.600. Only with arsenazo III does sexivalent uranium form a compound, the molar extinction coefficient of which has approximately the same value as that of the complex with chlorophosphonazo III (Table 1).

The main advantage of chlorophosphonazo III as a reagent for the photometric determination of sexivalent uranium, as compared with other reagents, is the insignificant, and sometimes complete absence of any interference from masking agents. Chlorophosphonazo III is better in this respect than the reagent arsenazo III suggested recently by Savrin [2]. Thus, when arsenazo III (taken in double the amount required for the formation of a complex) is used for the determination of 48.75 μg of uranium in a final volume of 50 ml, at pH 1.75, the presence of 2.5 mg of sodium ethylenediaminetetracetate (EDTA-Na) appreciably interferes with the determination, while no interference on the part of EDTA-Na could be observed during the determination of uranium by means of chlorophosphonazo III under the same conditions, even when 100 mg of EDTA-A was present. Sodium tartrate does not interfere with the determination of uranium by means of chlorophosphonazo III, while 50 mg of sodium tartrate leads to a decrease of more than 5% in the optical density when uranium is determined by means of arsenazo III.

Chlorophosphonazo III can be used for the determination of sexivalent uranium in the presence of 50 times its amount of fluorides (calculated as NaF) and 5000 times its amount of phosphates (calculated as NaH_2PO_4). The masking agents indicated interfere to a greater extent when arsenazo III is used under the same conditions; the permissible amounts of oxalates, fluorides and phosphates are 2.5-3 times less in this case.

As indicated above, chlorophosphonazo III reacts with many elements; nevertheless, on increasing the acidity of the solutions, the interaction of the reagent with some of these elements is reduced or ceases altogether. Thus, while cobalt, nickel, cadmium, manganese, and zinc react at pH 3.0 with chlorophosphonazo to form intensely colored compounds, at pH 1 only appreciable amounts of these elements give rise to an observable change in the color of the reagent.

TABLE 3

Determination of Uranium in Synthetic Mixtures of Uranium and Zirconium

Taken, mg		U found, mg	Relative experimental error for uranium, %
U	Zr		
25,6	74,4	26,1	+2,0
27,2	72,8	26,9	−1,1
30,7	69,3	30,2	−1,6
42,4	57,6	43,1	+1,6
48,5	51,5	48,2	−0,6

Table 3 contains the permissible ratios by weight of a number of elements with respect to uranium, when the solution whose color is being measured has a pH of 1, and whose uranium content is 1.0 μg/ml while the total reagent concentration is 1.75×10^{-5} M.

Th, Zr, Hf, Ce^{IV}, and Ti^{IV} interfere to the greatest extent. Nevertheless, even in these cases, sexivalent uranium can be determined in the presence of significantly greater amounts of these elements, as long as suitable masking agents are used (e. g., NH_4F for masking Zr and Hf, and H_2O_2 for Ti^{IV}) or these elements are reduced beforehand to their lower valence states (e. g., Ce^{IV} to Ce^{III}, Fe^{III} to Fe^{II}, and Sn^{IV} to Sn^{II}).

Photometric Determination of Uranium in its Alloys with Zirconium. 100 mg of the test alloy is dissolved in a platinum basin in 10 ml of dilute hydrochloric acid (1 : 1), 0.5 g of NH_4F (or the equivalent amount of NaF or HF) being added while the basin is heated on a water bath. The time taken for a sample to dissolve does not exceed 5 min even when the sample has only been roughly ground. When dissolution is complete, 20 ml of 0.1 M Na_2SiO_3 is added to complex the HF (to prevent damage to the glass vessel), and the solution transferred to a 250 ml standard flask, the basin is rinsed with 10-15 ml of dilute hydrochloric acid (1 : 1) and the washings combined with the main solution. After dilution to the mark with water, 1.00 ml of the solution obtained is transferred to a 100 ml standard flask, 5.0 ml of a monochloroacetate buffer solution is added (10 g $ClCH_2COONa$ and 20 g of $ClCH_2COOH$ in 1 liter of solution), followed by 2.5 ml of 0.1 M Na_2SiO_3 solution, 12.5 ml of 0.1 M NH_4F (or NaF) solution, and 2.00 ml of 0.001 M chlorophosphonazo III solution; the volume is made up to the mark with water and the optical density of the solution obtained is measured on a spectrophotometer in a cuvette with a layer thickness of 10 mm, at 670 mμ. The reference solution used is a solution containing the same amounts of chloroacetate buffer, Na_2SiO_3, NH_4F, and reagent, but not containing uranium and zirconium. The uranium content is determined from a calibration curve.

A calibration curve is constructed by introducing various amounts of a standard uranyl nitrate solution (containing 50, 100, 150, 200, and 250 μg U) into 100 ml standard flasks; monochloroacetate buffer solution, Na_2SiO_3, NH_4F, and reagent solutions are then added in the same amounts as those added to the test solution.

The method has been checked on synthetic mixtures made from metallic uranium and zirconium (Table 3).

The error does not exceed 2%. One determination takes about 15 min.

Synthesis of Chlorophosphonazo III. To 4.55 g (0.022 mole) of 2-amino-5-chlorobenzenephosphonic acid is added 60 ml of water and 4 ml of concentrated hydrochloric acid, the mixture is cooled on the outside with ice to 0-7°, and 1.7 g of sodium nitrite dissolved in 10 ml water added dropwise with stirring. The solution of 2-diazo-5-chlorobenzene phosphonic acid obtained is added to 4.5 g (0[illegible]mole) of chromotropic acid dissolved in 50 ml of a 10% sodium hydroxide solution. The pH of the mixture is [illegible]ted to about 9 and it is stirred for two hours, a solution of sodium hydroxide being added periodically in order to maintain the pH of the mixture within the limits 8-9. Concentrated hydrochloric acid is next added until the solution gives a strongly acid reaction to congo red paper; the product which separates out is filtered off, washed twice with 25% hydrochloric acid, and dissolved in 100 ml of 2% sodium hydroxide. The solution obtained is again acidified with concentrated hydrochloric acid until the solution gives a strongly acid reaction to congo red; the product which settles out is filtered off, washed twice with hydrochloric acid and dried at 80°. On increasing the drying temperature further to 160° the weight of the product decreases by 8.75% as the result of loss of water of crystallization; the loss corresponds to four molecules of water per molecule of chlorophosphonazo III.

The product obtained is a crystalline powder with an intense dark-red, almost black color. It is readily soluble in water, and is insoluble in benzene, chloroform, CCl_4, and ether. It is slightly soluble in acetone and somewhat more soluble in ethanol.

Found %: P 8.32; Cl 9.38; N 7.29.
Calculated %: P 8.20; Cl 9.36; N 7.42.

SUMMARY

A new, highly sensitive reagent for the photometric determination of sexivalent uranium is suggested; the reagent has been designated chlorophosphonazo III. The molar extinction coefficient of solutions of the compound of uranium with this reagent is 78.600 at 670 mμ. The high stability of the colored compound formed enables sexivalent uranium to be determined in the presence of large amounts of fluorides, phosphates, and oxalates. Sulfates, tartrates, and ethylenediaminetetracetic acid do not interfere with the determination of uranium, however much of them are present. A method has been developed for the direct photometric determination of uranium in its alloys with zirconium, Na_2SiF_6 being used for eliminating interference from the zirconium.

The synthesis of chlorophosphonazo III is described.

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THE EFFECT OF VANADIUM ON THE DETERMINATION OF URANIUM BY THE HYDROSULFITE-PHOSPHATE TITRIMETRIC AND PHOTOMETRIC METHODS

V. M. Brodskaya, G. A. Lanskoi, and V. G. Sochevanov

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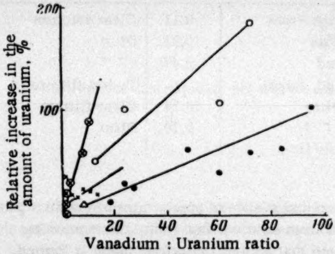
The titrimetric hydrosulfite-phosphate method of determining uranium was suggested by Volkov [1] and given a theoretical basis by Moiseev [1]. This method gives reliable results in many instances during the analysis of complex materials. Ponomarev [1] has developed a hydrosulfite-phosphate photometric method for the determination of small amounts of uranium.

During studies of the effect of various elements on the results of uranium determination by the titrimetric and photometric hydrosulfite-phosphate methods, it was found that vanadium leads to high results for uranium. As can be seen from Table 1, results of the titrimetric determination increase as a function of the relative amount of vanadium introduced by 10-85%; when the photometric variant is used the increase is doubled, reaching 190%. The higher the vanadium content, the greater the error. The absolute error also increases with increasing uranium content of the sample. In sample No. 2 which is poor in uranium, the relative error of the titrimetric error is about 50%, while in sample No. 1 which contains five times as much uranium, the relative error is 18-20%. The relative error is even smaller for samples containing 7% uranium.



The error in determining uranium as a function of the relative vanadium content of the sample.

This observation can be explained if one takes into account the quantitative ratio of uranium to vanadium in the test sample. The relation between the increase in the results for the uranium determination and the relative vanadium content in the original solution is shown in the diagram. Despite the large scatter of the experimental points, particularly at low uranium contents, there is nevertheless a general tendency for the results to increase with increases in the ratio V : U.

In order to make sure that the high results are not connected with the presence of vanadium, but also with the presence of uranium, the phosphates were precipitated in the presence of hydrosulfite from samples free from uranium, and from samples containing thorium instead of uranium. In all these experiments, vanadium was not observed to exert any influence, within the limits of experimental accuracy.

When the uranium is determined using a vanadometric finish, vanadium only interferes when it is present in the final solution in the trivalent state.

Vanadium was shown to be present in the phosphate precipitate experimentally.

TABLE 1

Results of the Determination of Uranium in Natural Samples as a Function of the Amount of Vanadium Introduced

Vanadium added	Sample No. 1				Sample No. 2				Sample No. 3	
	by the titrimetric method		by the photometric method		by the titrimetric method		by the photometric method		by the titrimetric method	
	found %	rel. dev., %	found %	rel. dev., %	found %	rel. dev., %	found, %	relative deviation %	found, %	relative deviation, %
0,0	0,609	0,0	0,610	0,0	0,083	0,0	0,081	0,0	6,95	0,0
10,0	0,651	7,0	0,736	21,0	0,089	9,9	0,133	52,0	—	—
20,0	0,696	14,3	0,800	30,0	0,101	21,7	0,162	100,0	—	—
30,0	0,693	13,6	—	—	0,093	14,8	—	—	7,50	8,0
40,0	0,699	14,8	0,968	59,0	0,124	53,1	0,165	103,0	—	—
50,0	0,730	19,8	—	—	0,103	27,2	—	—	—	—
60,0	0,721	18,4	1,169	92,0	0,120	48,1	0,235	191,0	7,66	10,2
70,0	0,716	15,5	—	—	0,123	51,3	—	—	—	—
80,0	0,738	21,2	—	—	0,150	85,2	—	—	—	—
90,0	—	—	—	—	—	—	—	—	8,38	19,9

TABLE 2

Calculation of the Values of the Oxidation–Reduction Potentials in the System V^V/V^{IV} as a Function of the Acidity and the Concentration Ratios of the Vanadium Ions

pH	Oxidation-reduction potential		
	$V^V/V^{IV} = 1$	$V^V/V^{IV} = \frac{1}{10}$	$V^V/V^{IV} = \frac{1}{100}$
0	+1,0	+0,942	+0,884
1	+0,884	+0,826	+0,768
2	+0,768	+0,710	+0,652
3	+0,652	+0,594	+0,536
4	+0,536	+0,478	+0,420
5	+0,420	+0,362	+0,304
6	+0,304	+0,246	+0,178

TABLE 3

Effect of pH of the Solution on Oxidation of Quadrivalent Vanadium Ions by Ferric Ions

Established pH of the solution	External appearance of the solution	Optical density	Note
1.7	Light-rose	0.11	Clear solution
2.0	Rose	0.21	Ditto
3.0	Red	0.67	" "
5.0	Red, turbid	?	Turbid filtrate
7.4	Ditto	0.74	Clear filtrate
9.0	" "	0.70	Ditto

X-ray structural studies of precipitates of uranium phosphates separated from solutions free from, and containing vanadium, showed that no new crystalline phase is formed. The fact that the x-ray spectrograms were completely identical, coupled with the large difference in the ionic radii of U^{IV} and V^{III} excludes the phenomenon of isomorphism. It only remains to suggest the occurence of selective adsorption of trivalent vanadium compounds in an amorphous form on the surface of the phosphate precipitate of quadrivalent uranium. This assumption agrees with the fact which we have established, that it is possible to remove vanadium from the phosphate precipitate by means of a solution of an oxidizing agent (see below) which has a low redox potential.

A comparison of the normal oxidation–reduction potentials of an acid solution of hydrosulfite, and of solutions containing vanadium in its various oxidation forms, shows that quinque- and quadrivalent vanadium should be reduced by hydrosulfite in an acid medium to its trivalent state. This phenomenon should also occur in weakly acid solutions.

In order to calculate the standard potential of a system in which oxidation of hydrosulfite in an acid medium

TABLE 4

Results of Titrimetric Determination of Uranium after Washing the Phosphate Precipitate with Iodine

Uranium taken, mg	Uranium found after treating the phosphates of U^{IV} with iodine, mg	Absolute deviation, mg
0,5	0,49	−0,01
1,0	1,0	±0,00
2,0	1,94	−0,06
5,0	5,02	+0,02
7,0	7,00	±0,00

occurs, using the results for the free energy of the hydrosulfite ion, Latimer [3] used the following equation for the reaction: $HS_2O_4^- + H_2O = 2H_2SO_3 + H^+ + 2e$.

It is not difficult to show that, according to this equation, the relation between the oxidation potential and the pH of the solution should conform to the equation:

$$E = E_0 + \frac{0,058}{2} \lg \frac{[H_2SO_3]^2}{[HS_2O_4]} - 0,029 \text{ pH},$$

where E_0 is the normal oxidation−reduction potential of the solution, and equal to 0,08 v [3].

For the reduction of quadrivalent vanadium $VO^{2+} + 2H^+ + e = V^{3+} + H_2O$ the relation between the oxidation−potential and pH is of the form:

$$E = E_0 + 0,058 \lg \frac{[VO^{2+}]}{[V^{3+}]} - 0,116 \text{ pH},$$

where E_0 is the normal oxidation−reduction potential, and is equal to 0.361 v [3].

Using the relationships indicated, it is possible to calculate the pH value, at which the hydrosulfite will not reduce the V^{IV} ions further; this is known to occur only when the oxidation−reduction potentials of both systems become equal to one another, i. e., E = E.

In order to be able to use the values of the normal oxidation−reduction potentials directly, it was arbitrarily assumed that the ratio of the concentrations of the oxidized to the reduced forms in the test solution is equal to unity, i. e.,

$$\frac{[VO^{2+}]}{[V^{3+}]} = 1 = \frac{[H_2SO_3]^2}{[H_2SO_4^-]}$$

In this case the requisite pH will be equal to:

$$\text{pH} = \frac{E_0 - E_0}{0,116 - 0,029} = \frac{0,44}{0,087} = 5,06.$$

Thus, even in weakly acid solutions having a pH below 5, the quadrivalent vanadium ions should be reduced by more than 50% to the trivalent state by the hydrosulfite.

Since it has a low solubility, the phosphate of V^{III} separates out with the precipitate of uranium phosphate and sulfur, and thereby increases the titration results (see Table 1). When such a precipitate is washed on the filter with the "normal" wash liquor, the vanadium compound is not completely removed from it.

Vanadium interferes to an even greater extent during the photometric determination of uranium.

This observation led us to look for the reasons for the high results, not only in the reducing action of trivalent, but also in that of quadrivalent vanadium.

The main oxidation−reduction process in the photometric variant of the method is expressed by the equation: $U^{VI} + 2Fe^{III} = U^{VI} + 2Fe^{II}$.

Trivalent vanadium ions present in solution increase the concentration of ferrous ions according to the euqation: $V^{III} + Fe^{III} = V^{IV} + Fe^{II}$.

There is no doubt that oxidation of trivalent vanadium by ferric ions occurs, since the normal oxidation−reduction potential of the system V^{IV}/V^{III} is considerably lower than the potential of Fe^{III}/Fe^{II}. It is usually

TABLE 5

Effect of Washing the Phosphate Precipitates with Iodine Solution on the Vanadium Content of these Precipitates (6.1 mg U + 50 mg V)

Washing			
with iodine solution		water	
Vanadium found, mg			
in the precipitate	in the filtrate	in the precipitate	in the filtrate
0,0	0,480	0,336	0,0
0,0	0,154	0,160	0,0
0,0	0,154	0,112	0,0

accepted that in acid media, oxidation of vanadium is limited by the formation of quadrivalent vanadium ions. In order to explain this,we were compelled to assume that under the conditions used in the analysis, on switching over from strongly acid to neutral solutions the following process occurs: $V^{IV} + Fe^{III} = V^{V} + Fe^{II}$, which, according to [5], proceeds quantitatively in weakly alkaline and alkaline media.

That this process can, theoretically, occur, follows from an examination of the relationship between the oxidation–reduction potential of V^{V}/V^{IV} and the acidity of the solution. Actually:

$$3H_2O + VO^{2+} \rightleftarrows V(OH)^{+} + 2H^{+} + e$$

$$\pi = \pi_0 + 0{,}058 \lg \frac{[V(OH_4)^{+}]}{[VO^{2+}]} - 0{,}116\,pH,$$

where π_0 is the normal oxidation–reduction potential equal to +1.0 v [3].

Table 2 contains the calculated values of the oxidation–reduction potentials of the system V^{V}/V^{IV} at various ratios of V^{V}/V^{IV} and various pH's of the solution.

By comparing the results given in Table 2 with the value of the normal oxidation–potential Fe^{III}/Fe^{II}, which is equal to +0.77 v, it is not difficult to see that under the most unfavorable conditions $V^{V}/V^{IV} = 1$, oxidation of quadrivalent vanadium to its quinquevalent state by ferric ions can occur even at pH 2. In those cases where quadrivalent vanadium ions predominate, oxidation may even be observed at pH 1. The possibility of oxidation increases when excess ferric ions are present, or when a material such as α,α'-dipyridyl is present, which can complex ferrous ions into a stable complex.

Oxidation of quadrivalent vanadium by ferric ions should be particularly marked at pH 2-4, since up to pH 4 (i. e., up to the beginning of hydrolysis of ferric iron) the value of the oxidation–reduction potential of Fe^{III}/Fe^{II} is almost independent of the pH.

The possibility of the oxidation of quadrivalent vanadium ions by ferric ions in a weakly acid medium was shown experimentally. A solution of the sulfate of quadrivalent vanadium containing 1 mg of vanadium was added to a decinormal solution of sulfuric acid; a sulfuric acid solution containing 5 mg of ferric iron was then added. The solutions,which had a volume of about 50 ml,were neutralized with tetraborate solution to a given pH value which was controlled by means of a pH-meter. To the solutions prepared in this way were added 2.5 ml lots of 0.5% α,α'-dipyridyl solution which interact with ferrous ions [4]. The optical density of the ferrodipyridyl solutions was measured on a FEK-M photocolorimeter.

Similar experiments were carried out in which no ferric salt solution was added; after addition of the α,α'-dipyridyl,all the solutions were colorless, showing thereby that α,α'-dipyridyl does not react with vanadium ions, and also showing the absence of ferrous ions; when a solution of ferrous iron was added, as a control, a color developed immediately.

Table 3 illustrates the reducing action of quadrivalent vanadium ions on ferric ions. Starting from pH 1.7 a rose color appears as a result of the formation of ferrous ions; this color almost reaches its limiting value at a pH as low as 3.

These experiments therefore demonstrate the reducing properties of quadrivalent vanadium with respect to ferric ions, not only in alkaline, but also in weakly acid media.

In order to eliminate interference from vanadium, it should be removed from the phosphate precipitate by washing the latter with a solution of oxidizing agent which is a weak one with respect to tri- and quadrivalent vanadium, and which will not affect the phosphate of quadrivalent uranium. As long ago as 1954 we suggested iodine solutions for this purpose.

TABLE 6

Results of Determination of Uranium in Natural Samples (With added Vanadium) after Washing the Phosphate Precipitates with Iodine Solution

Vanadium added, mg	Sample No. 1				Sample No. 2				Sample No. 3	
	found, %				found, %				found, %	
	titrimetrically		photometrically		titrimetrically		photometrically		titrimetrically	
	with iodine treatment	with iodine treatment	with iodine treatment	with iodine treatment	with iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment
0,0	0,609	0,611	0,609	0,610	0,081	0,081	0,080	0,081	—	—
10,0	0,605	0,651	0,612	0,736	0,081	0,089	0,081	0,133	6,95	6,96
20,0	0,615	0,695	0,614	0,800	0,081	0,101	0,088	0,162	—	—
30,0	0,608	0,693	—	—	0,084	0,093	—	—	6,90	7,50
40,0	0,610	0,699	0,612	0,968	0,087	0,124	0,096	0,165	—	—
50,0	0,606	0,730	—	—	0,082	0,103	—	—	—	—
60,0	0,610	0,721	0,614	1,169	0,084	0,120	0,097	0,235	6,97	7,66
70,0	0,611	0,716	—	—	0,086	0,123	—	—	—	—
80,0	0,617	0,738	—	—	0,088	0,156	—	—	—	—
90,0	—	—	—	—	—	—	—	—	7,02	8,33

Oxidation of trivalent vanadium by iodine was carried out by additional washing of the phosphate precipitate on the filter.

The treatment of the precipitate with iodine solution also proved useful from another point of view, since iodine oxidizes any hydrosulfite decomposition products.

Table 4 contains results for the determination of uranium in synthetic solutions after the phosphate precipitate has been washed with iodine.

The following experiments were carried out in order to show that washing the phosphate precipitate with iodine solution leads to oxidation of any vanadium in this precipitate, and facilitates its removal. Equal amounts of uranium and vanadium, in two parallel samples, were treated under identical conditions with hydrosulfite, and were precipitated as their phosphates. The precipitates were transferred onto filters, and, as usual, were carefully washed with acidified water until the wash liquors gave a negative reaction with potassium permanganate. The first sample was then given an additional wash with an iodine solution having a pH of 5.

The second, parallel sample, was given an additional wash with the same volume of acidified water. Both of the precipitates on the filters, and both the filtrates obtained were analyzed for their vanadium content.

The results obtained (Table 5) leave no doubt regarding the removal of the vanadium from the precipitate.

The possibility of removing interference, even from large amounts of vanadium, during titrimetric and photometric determination of uranium, by washing the phosphate precipitate with iodine solution is illustrated by the results given in Table 6.

What was still not clear was the way the iodine eliminates interference from quadrivalent vanadium which may be formed as the result of incomplete oxidation of the trivalent vanadium contaminating the precipitate of quadrivalent uranium phosphate.

A comparison of the normal oxidation potential of iodine, equal to +0.536 v [3], with the potential of vanadium (Table 2) shows that at pH's above 4, iodine solutions should oxidize vanadium compounds to the quinquevalent state. The conclusion was confirmed experimentally.

Mixtures were prepared, each containing 1 mg V^{IV} + 50 ml water + 0.1 ml of a 0.1 N solution of iodine in potassium iodide + 2 ml of a 0.5% starch solution. All the reagents apart from the solution of a quadrivalent vanadium compound were used in parallel experiments. All the solutions had an intense blue color when the mixtures were acid (pH 2-3.7). On adding sodium tetraborate to the solutions containing quadrivalent vanadium to adjust the pH to a definite value, it was found that the blue color disappeared at pH's above 4. Solutions which did not contain vanadium kept their blue color over the range pH 2.0-9.3.

Thus, as the quinquevalent vanadium compound is formed as the result of oxidation with iodine, it is washed out from the precipitate by the aqueous solution of iodine having a pH of 5.0-5.5.

The work carried out makes it possible to improve the titrimetric [6, 7] and the indirect photometric [2] methods of determining uranium in mineral raw material of complex composition.

SUMMARY

It has been shown that the high results obtained during the determination of uranium by the hydrosulfite-phosphate method when vanadium is present, can be ascribed to the adsorption of lower vanadium compounds by uranium (IV) phosphate.

It is suggested that interference on the part of vanadium can be eliminated by washing the phosphate precipitate with iodine solution.

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INTERACTION IN THE SYSTEM PALLADIUM-DIMETHYL-GLYOXIME-TRIVALENT IRON

Z. G. Golybtsova, L. I. Lebedeva, and Yu. V. Morachevskii

A. A. Zhdanov Leningrad State University

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Various oximes are widely used in the analytical chemistry of palladium for its gravimetric and photometric determination [1-4]. Many of these oximes permit palladium to be determined in the presence of a number of other elements, and to be separated from interfering elements. Nevertheless, ferric ions, when present in solution, often interfere with the completeness of the separation of palladium by oximes [5-7]. During the interaction of palladium ions with dimethylglyoxime in perchloric and nitric acid solutions, ferric ions, under certain conditions, can completely prevent formation of palladium dimethylglyoximate precipitate [8]. Under these conditions the solution has a dark-brown color. We have established earlier [9] that trivalent iron forms a soluble complex compound with dimethylglyoxime in acid media.

It might be assumed that in a solution containing palladium, dimethylglyoxime, and trivalent iron, interaction may occur with formation of a ternary compound.

Published information only relates to numerous attempts to decrease the influence of trivalent iron by masking the latter with various reagents. All these attempts, however, are purely empirical in nature, since there is no information on the composition of the ternary complex formed, its stability, and the stability limits, which is related to the latter.

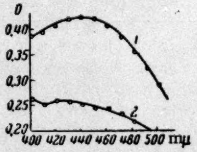

Fig. 1. Absorption curves of solutions of the ternary complexes for various ratios of Pd : H_2Dm : Fe^{III}. 1) Pd : : H_2Dm = 1 : 2, Fe^{III} in excess; 2) Pd : H_2Dm : Fe^{III} = = 1 : 2 :1.

We have tried to obtain the information which is lacking.

Optical density was measured on a SF-4 spectrophotometer. The hydrogen ion concentration was determined with a glass electrode.

The fact that the optical densities of the individual components of a solution containing simultaneously dimethylglyoxime, palladium and ferric ions are not additive confirmed our assumption to the formation of a ternary compound. In Fig. 1 (Curve 1) is shown the absorption curve of a solution in which $C_{Pd} = 9.5 \times 10^{-5}$ g·atom/liter, $C_{Fe^{III}} = 1.4 \times 10^{-3}$ g·atom/liter, $C_{H_2Dm} = 1.9 \times 10^{-4}$ M. The individual components of this solution, when taken separately, hardly absorb light at all at the given concentrations and pH, over the wavelength region examined.

In order to determine the composition of the compound formed in solution, it was necessary to combine various spectrophotometric methods.

The ratio between palladium and dimethylglyoxime was determined by the isomolar series method, the amount of trivalent iron being kept constant, and in a large excess with respect to palladium.

Fig. 2 illustrates the results obtained in experiments carried out at a wavelength of 440 mμ for two isomolar series with total concentrations of palladium ions and dimethylglyoxime of 8×10^{-5} M and 1.6×10^{-4} M, and a pH of 2.10. The curves for the deviation of the measured optical densities from additivity have a maximum at a ratio of the components Pd : H_2Dm = 1 : 2. We obtained similar results in a series in which the total concentration of palladium and trivalent iron was kept constant while the dimethylglyoxime concentration was varied (Fig. 3). A hundredfold excess of trivalent iron was taken with respect to palladium, the pH was 2.23. The ratio Pd : H_2Dm was found to be 1 : 2; the optical density of the solutions did not change, starting at a twofold excess of dimethylglyoxime.

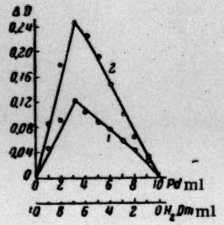

Fig. 2. Deviation of the optical density from additivity on the ΔD−solution composition curve, for a constant excess of trivalent iron. 1) C = $8 \cdot 10^{-5}$ M; 2) C = $= 1.6 \cdot 10^{-4}$ M.

The stoichiometric coefficient of trivalent iron in the ternary complex was determined relative to palladium. It was established that when certain conditions are observed, namely, careful addition (dropwise) of the solution of a palladium salt to the solution containing dimethylglyoxime and trivalent iron in a molar ratio of 2 : 1, it is possible to avoid formation of palladium dimethylglyoximate. In this way we succeeded in obtaining a compound with the ratio Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 in solution. Preparation of such a compound at palladium concentrations of the order of 10^{-5} - 10^{-4} g·atom/liter is only possible at pH 3-4.5. Below pH 3 palladium dimethylglyoximate separated out, while at pH > 4.5 ferric hydroxide started to separate out.

The absorption curve of this solution in which $C_{Pd} = 9.5 \times 10^{-5}$ g · atom/liter, $C_{H_2Dm} = 1.9 \times 10^{-4}$ M, and $C_{Fe^{III}} = 9.5 \times 10^{-5}$ g·atom/liter, at pH 3.20, differs slightly from the absorption curve of the solution obtained when trivalent iron is present in excess with respect to palladium (Fig. 1, Curve 2). The absorption maximum is shifted slightly towards the short wavelength side of the spectrum.

The nature of the changes in the optical density of solutions in a series of experiments in which the palladium and dimethylglyoxime concentrations were kept constant at a ratio of 1 : 2, while the concentration of trivalent iron was increased, indicates possible formation of a more complex compound in the system. The optical density of solutions with increasing trivalent iron concentrations increases continuously, and only becomes constant when the iron is present in a considerable excess with respect to palladium (Fig. 4).

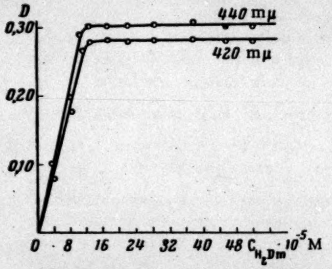

Fig. 3. The relation between the optical density of the solutions and the dimethylglyoxime concentration for constant concentrations of palladium and trivalent iron. $C_{Pd} = 5.8 \cdot 10^{-5}$ M; $C_{Fe^{III}} = 5.8 \cdot 10^{-3}$ M.

In order to determine the stoichiometric coefficient of trivalent iron in the compound formed in the presence of excess iron, we used the "equilibrium shift" method [10]; we modified this method slightly in order to apply it under our experimental conditions*. Bearing in mind the possibility that complexes having different iron contents may be present in solution at the same time, we tried to determine the concentration of each of them under conditions such that

$$D_{solution} = \epsilon_2 X_1 + \epsilon_2 X_2, \qquad (1)$$

$$C_{Pd} = X_1 + X_2 + P, \qquad (2)$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of the complexes; X_1 and X_2 are the equilibrium concentrations of the complexes; and P is the palladium concentration in solution, which is determined by the solubility of palladium dimethylglyoximate under the given conditions.

The molar extinction coefficients of the higher complex (ϵ_2) were determined in solutions containing a hundredfold excess of trivalent iron.

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* We regarded this second process as a case of stepwise complex formation, i. e., formation of a more complex ternary compound from the simpler compound which has a ratio of Pd : H_2Dm : Fe^{III} = 1 : 2 : 1.

We calculated the molar extinction coefficients of the complex in which the ratio of the components is Pd : H_2Dm : Fe^{III} = 1 : 2 : 1, on the basis of the optical densities of solutions of this compound, taking into account that the equilibrium concentration of the complex in the given instance is equal to the difference $C_{Pd} - P$.

According to our results*, at pH 3 and at room temperature, $P = 4.3 \times 10^{-8}$ g · atom/liter, which gives the following mean values for the molar extinction coefficient:

ε_1	ε_2
$\varepsilon_{440} = 2627 \pm 05$	$\varepsilon_{440} = 5161 \pm 45$
$\varepsilon_{470} = 2428 \pm 27$	$\varepsilon_{470} = 4694 \pm 20$
$\varepsilon_{500} = 1926 \pm 30$	$\varepsilon_{500} = 3531 \pm 20$

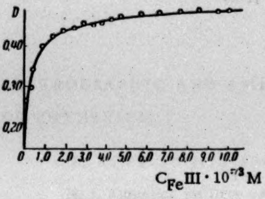


Fig. 4. The relation between the optical density and trivalent iron concentration when the palladium and dimethylglyoxime concentrations are constant. $C_{Pd} = 9.5 \cdot 10^{-5}$ M; $C_{H_2Dm} = 1.9 \cdot 10^{-4}$ M; λ = 440 mμ; l = 10 cm.

Having solved equations (1) and (2), and determined the mean values of X_1 and X_2 on the basis of optical density measurements in three parts of the spectrum, we constructed a curve within the coordinates log X_2/X_1, log [Fe^{III}]. As shown in Fig. 5, tangent $\alpha = 1$, this indicates that in increasing the trivalent iron concentration, a further ion of Fe^{III} adds on to the simpler complex in which the ratio of the components is Pd : H_2Dm : Fe^{III} = 1: 2 : 1 to form a second compound in which Pd : H_2Dm : Fe^{III} = 1 : 2 : 2.

We can only assess the stability of the compound formed approximately. The first stepwise instability constant, determined graphically by the "equilibrium shift" method, was found to be of the order of 10^{-3} (Fig. 5).

As for the second stepwise instability constant, we can only say that it should be of an order not greater than 10^{-9}, when one bears in mind that the limiting equilibrium concentrations of trivalent iron and palladium in solution are determined by the value of the solubility of palladium dimethylglyoximate at the given hydrogen ion concentration, otherwise, a precipitate of palladium dimethylglyoximate would be formed.

In alkaline solutions obtained on adding either ammonia or the caustic alkalis, no interaction was observed between dimethylglyoxime palladium, and trivalent iron. At a ratio of Pd : H_2Dm : Fe^{III} = 1:2:1 a precipitate of ferric hydroxide formed; when excess dimethylglyoxime was present, ferric hydroxide was not precipitated because of the formation of ferric dimethylglyoximate [9, 11, 12].

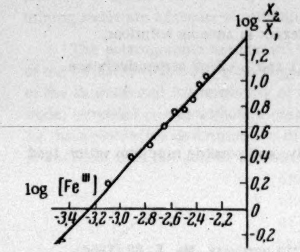
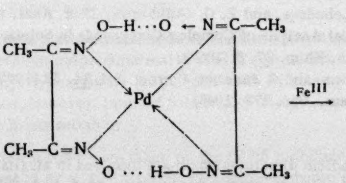


Fig. 5. Determination of the stoichiometric coefficient of iron by the "equilibrium shift" method.

On the basis of the results obtained, the following possible ways in which the ternary compound is formed can be suggested. Presumably, trivalent iron, on reacting with palladium dimethylglyoximate in an acid medium, successively replaces the hydrogen ion of the oxime group according to the following scheme:



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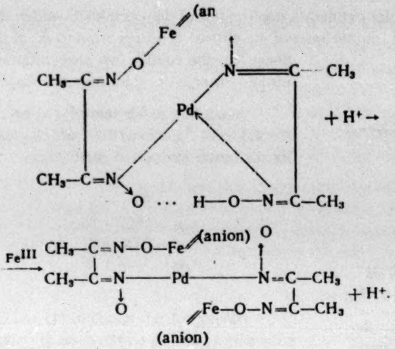
* Since the requisite data could not be found in the literature, we determined the solubility of palladium dimethylglyoximate in 0.5, 1.5, and 2 N $HClO_4$ solutions at room temperature, and found the solubility at pH 3 and pH 2 by extrapolation.



It is probable that substitution of hydrogen by trivalent iron is connected with the simultaneous destruction of the coordination bond between palladium and the oxime group. This assumption follows from the fact that palladium dimethylglyoximate dissolves in alkalis.

Excess OH^- ions favors a weakening of the H−O bond in the oxime group; the hydrogen bond is destroyed and makes the substitution of H^+ by an alkali metal possible. The formation of a compound which is readily soluble in water is probably connected with the destruction of the coordination bond in the molecule.[*]

SUMMARY

It has been shown that palladium, dimethylglyoxime, and iron can interact in aqueous solutions.

Two ternary compounds in which the ratio Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 and 1 : 2 : 2 respectively are formed in weakly acid media.

Ternary compounds are not formed in alkaline media.

The stability of the compounds formed has been assessed approximately, and possible reactions which lead to their formation have been outlined.

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[*] Feigl assumes [13] that when palladium dimethylglyoximate dissolves in alkalis, an inner complex anion is formed, so that he regards palladium dimethylglyoximate as a compound which functions as an inner complex salt in neutral and acid solutions, and as an acid in alkali solutions.

POLAROGRAPHIC AND AMPEROMETRIC DETERMINATION OF RUTHENIUM

N. K. Pshenitsyn and N. A. Ezerskaya

N. S. Kurnakov Institute of General and Inorganic Chemistry,
Academy of Sciences, USSR, Moscow

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Most of the published methods for the polarographic determination of ruthenium [1] cannot be included in a general scheme of analysis for the platinum metals. The reason for this is either the impossibility of converting all the ruthenium quantitatively into a compound suitable for polarographic determination [2, 3], the instability of the ruthenium compound chosen for its polarographic determination [4], the impossibility of determining moderate amounts of ruthenium ($10^{-3}-10^{-5}$ M) [5, 6], or the insufficient sensitivity of the method [7].

The polarographic method [8] which we suggested earlier for the determination of ruthenium on the basis of the reduction wave of $K_4Ru_2OCl_{10}$ on a platinum electrode, also has a number of disadvantages. As a result of the slowness and irreversibility of the electrode reaction for the reduction of $[Ru_2OCl_{10}]^{4-}$ on a rotating electrode, extended curves without a clear cut diffusion current region are obtained, which cannot be recommended for the quantitative determination of ruthenium. The use of a stationary electrode also has its drawbacks, and, in addition, does not permit determination of less than 5 μg Ru/ml. Platinum, palladium, iridium, gold, and dissolved oxygen should interfere with polarographic determination of ruthenium. More recently [9] we have found a simple method of preparing solutions of sodium hexachlororuthenate (Na_2RuCl_6), which is reversibly reduced on a platinum electrode, and which gives clearly defined waves with $E_{1/2}$ equal to 0.72 v (with respect to the saturated calomel electrode) (Fig. 1) on both stationary and rotating platinum electrodes. Experiments have shown that solutions of sodium hexachlororuthenate in 6 N hydrochloric acid are fairly stable. The polarographic wave of $[RuCl_6]^{2-}$ corresponds to its reduction to $[Ru(H_2O)Cl_5]^{2-}$. As a result, the platinum electrode is not contaminated by metal which might separate out during reduction, and there is no need for special cleaning operations, which appreciably simplifies its use. All these advantages led us to use hexachlororuthenate for the polarographic determination of ruthenium.

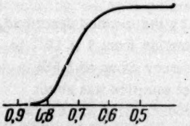

Fig. 1. Polarographic curve for Na_2RuCl_6.

$[RuCl_6]^{2-}$ ions are reduced on a platinum electrode in the same potential range as $[IrCl_6]^{2-}$ ions. Accordingly, we tried to titrate ruthenium amperometrically with the same reducing agent which we used earlier for the titration of iridium, namely, hydroquinone [10]. Apart from hydroquinone, ascorbic acid can also be used for titrating ruthenium. Since, however, standard solutions of ascorbic acid do not keep well (their factors change with time), ascorbic acid is less suitable.

Apparatus and Reagents. Polarograms were taken on the LP 55 instrument (a Czech instrument) with a galvanometer whose sensitivity was 3.52×10^{-3} μa/mm for anodic-cathodic polarization. The galvanometer readings were read off visually on an extension scale 40 cm long with the zero at the middle. The voltage was altered manually. The cathode was a rotating platinum electrode 5 mm long, 0.5 mm in diameter. This electrode was rotated at the rate of about 800 rpm. A saturated calomel electrode with a large mercury surface (35 mm in diameter) was used as the anode. The volume of the electrolytic cell was 20 ml. Amperometric titration was carried out in the same apparatus as that used for taking polarograms. The titrant solution was added from a microburet with scale divisions of 0.02 ml. A standard ruthenium solution (T = 0.03 and 0.103 mg/ml) was prepared from the distillate obtained on distilling RuO_4; the RuO_4 was distilled from a sulfuric acid solution by means of sodium bromate, and absorbed in hydrochloric acid. The distillate was evaporated almost to dryness, it was then boiled with 2 N hydrochloric acid and diluted with 2 N HCl to the requisite volume. The solution was standardized gravimetrically by means of thionalide.

The hydroquinone solutions used as the titrant were prepared by dissolving accurately weighed aliquots of the commercial reagent. In order to increase the stability of these solutions, they were prepared in twice distilled water, and 10 ml hydrochloric acid added per liter. The solutions were standardized by amperometric titration with the Na_2IrCl_6 solution. Periodic checks on the factor of the solutions, showed that solutions of hydroquinone prepared as described, are stable for more than two months. Simon and Zyka [11], in some work which they carried out specially for this purpose, also demonstrated the high stability of hydroquinone solutions. Hydroquinone solutions, 1 ml of which corresponded to 0.1, 1.0, and 5.0 mg of ruthenium respectively were used as titrants.

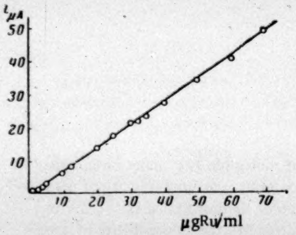

Fig. 2. The relation between the diffusion current and ruthenium concentration.

Polarographic Determination of Ruthenium. The technique used for preparing the Na_2RuCl_6 solutions in order to take polarograms was as follows:

The solution containing a mixture of the various complex chlorides of ruthenium was evaporated to dryness on a water bath, after having added a small amount of sodium chloride. Five ml of 0.8-1.0 N HCl and 5-6 drops of hydrogen peroxide were then added, and the solution heated until the solution was colorless or had a slight rosy-yellow color (for ruthenium contents greater than 80 μg/ml). $Na_2Ru(H_2O)Cl_5$ is thereby formed. An equal volume of concentrated hydrochloric acid was added and heating continued on a water bath until only a moderate amount of bubbles came off. The solution of Na_2RuCl_6 was boiled on a hot plate for 5 min to remove chlorine, it was rapidly cooled, diluted with hydrochloric acid (1 : 1) to 10 ml, and polarograms taken over the range +0.9 to +0.5 v.

The polarograms obtained for solutions with various ruthenium contents, prepared by the method described, showed that the diffusion current of quadrivalent ruthenium is proportional to its concentration from 1×10^{-5} to 2×10^{-3} M (from 1 to 200 μg/ml) (Fig. 2). This proportionality is observed with an accuracy of up to 1.5%. The reproducibility of the diffusion currents obtained when taking polarograms of parallel samples was about 2.5% for samples containing 1-10 μg Ru/ml, while for higher Ru concentrations, the reproducibility was 0.5 %. The minimum amount of ruthenium which can be determined is 1 μg/ml. The accuracy of the method is not high enough for taking polarograms of solutions containing more than 200 μg Ru/ml. The error in these cases may arise during preparation of the solutions, since at high Ru concentrations it is difficult to decide on the completeness of the conversion into $Na_2Ru(H_2O)Cl_5$ from the change in the color of the solution, during the interaction of the original solution with hydrogen peroxide. Accordingly, during determination of large amounts of ruthenium, it is best to taken an aliquot of the solution. Chlorine is formed during the preparation of $[RuCl_6]^{2-}$ by the interaction of 6 N HCl with hydrogen peroxide. In the presence of chlorine, the first part of the polarogram of quadrivalent ruthenium is strongly distorted; chlorine must therefore be removed from the solution. A stream of carbon dioxide can be used for this purpose. Such a method, however, takes a long time—up to 40 min. We therefore removed chlorine by boiling the solution. Since gradual reduction of Ru^{IV} occurs on heating Na_2RuCl_6 solutions, the time for which solutions are boiled should not exceed 5 min for solutions containing hundredths of a milligram in 10 ml. More concentrated solutions can be boiled for 10-12 min.

Measurements of the wave height for Na_2RuCl_6 solutions carried out at different temperatures, showed that the diffusion current of quadrivalent ruthenium increases by approximately 2% per degree. Nevertheless, since on prolonged heating partial reduction of $[RuCl_6]^{2-}$ occurs, the actual increase of the diffusion current with

TABLE 1

Amperometric Titration of Na_2RuCl_6 with Hydroquinone

Ru, mg		Absolute error, mg	Relative error, %	Ru, mg		Absolute error, mg	Relative error, %	Ru, mg		Absolute error, mg	Relative error, %
taken	found			taken	found			taken	found		
0,95	0,92	—0,03	—3,1	0,20	0,21	+0,01	+5,0	0,040	0,039	—0,001	— 2,5
0,80	0,82	+0,02	+2,5	0,10	0,10	0	0	0,020	0,021	+0,001	+ 5,0
0,70	0,68	—0,02	—2,8	0,090	0,090	0	0	0,010	0,009	—0,001	—10,0
0,50	0,50	0	0	0,070	0,071	+0,001	+1,4	2,00	1,91	—0,09	— 4,7
0,40	0,40	0	0	0,060	0,059	—0,001	—1,7	4,00	4,24	+0,24	+ 3,0
0,30	0,29	—0,01	—3,3	0,050	0,049	—0,001	—2,0	6,00	5,62	—0,38	— 6,3

TABLE 2

Determination of Ruthenium in Industrial Products

Material	Ru determined, %			
	gravimetrically	photometrically	potentiometrically	amperometrically
№ 1	0,027	—	—	0,026
№ 2	0,048	0,042	—	0,046
№ 3	—	0,21	—	0,19
№ 4	2,16	—	2,11	2,12

temperature is considerably higher. Having determined $[RuCl_6]^{2-}$ in solution, after heating the solutions to 40-50°, we calculated that the temperature coefficient of the diffusion current of $[RuCl_6]^{2-}$ as equal to 3.3% per degree. This significant change in current with temperature must be borne in mind during the polarographic determination of ruthenium. In order to avoid temperature effects, immediately after taking polarograms of a test solution, we took polarograms of a standard solution prepared at the same time. The amount of ruthenium was determined by comparison with the standard solution. Another method which can be recommended is thermostatting of the electrolytic cell, and determination of the ruthenium from a calibration curve obtained at a definite temperature.

When solutions of Na_2RuCl_6 are allowed to stand for a long time, gradual reduction to $Na_2Ru(H_2O)Cl_5$ occurs. Test solutions should not therefore be kept for a long time. Experiments have shown that polarograms of dilute solutions (1-10 μg Ru/ml) should be taken not later than 45 min after their preparation. More concentrated solutions can be kept without any changes for several hours.

Large amounts of rhodium, platinum, palladium, and osmium do not interfere with the polarographic determination of ruthenium, since the complex chlorides of these elements are reduced at appreciably more negative potentials. Iridium interferes, since the half-wave potential of $[IrCl_6]^{2-}$ is about 0.7 v. $[AuCl_4]^-$ starts to be reduced at +0.5 v, and therefore gold does not interfere in small amounts. On increasing the gold concentration, the area of the limiting current of ruthenium decreases, and when the amount of gold present is 15 times that of the ruthenium, determination of the latter becomes very difficult. Copper, nickel, selenium, and tellurium do not affect the ruthenium polarographic wave. Trivalent iron starts to be reduced at +0.5 v, and when the iron present is ten times the ruthenium, the iron wave fuses with the ruthenium wave. Large amounts of iron also complicate ruthenium determination because of the formation, during preparation of the solution, of ferrous ions which reduce the quadrivalent ruthenium. In order to oxidize all the ferrous iron it is necessary to add a large amount of hydrogen peroxide and carry out the oxidation in a more acid medium, otherwise the ruthenium results are low. Atmospheric oxygen does not interfere so that open electrolytic cells can be used. It was particularly important to establish the effect of sulfur dioxide, since in many of the analytical schemes adopted for the analysis of ruthenium, the latter is separated from all remaining elements in the form of its tetroxide which is absorbed by hydrochloric acid saturated with sulfur dioxide. When a distillate obtained in this way is evaporated to dryness and then subjected to all the operations described above for converting the ruthenium into Na_2RuCl_6, low results are always obtained for ruthenium. The reason for this is that probably some of the ruthenium forms complex sulfite- or sulfate compounds, which, even in dilute hydrochloric acid solutions are oxidized by hydrogen peroxide to the volatile tetroxides. It is therefore essential to destroy these compounds carefully by repeated evaporation of the solution with concentrated hydrochloric acid in the presence of sodium chloride.

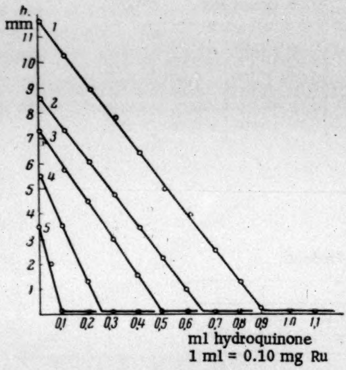

Fig. 3. Curves obtained during the amperometric titration of ruthenium with hydroquinone. 1) 0.90 mg Ru; 2) 0.70 mg Ru; 3) 0.50 mg Ru; 4) 0.25 mg Ru; 5) 0.10 mg Ru.

Conversion of all the ruthenium into Na_2RuCl_6 is much easier when, during the distillation of RuO_4, hydrochloric acid saturated with sulfur dioxide is used only in the last receivers. The contents of the last receivers which only contain a small amount of the ruthenium must be evaporated several times with hydrochloric acid, and only after this stage, combined with the contents of the first receivers which do not contain any sulfur dioxide.

Amperometric Titration of Ruthenium with Hydroquinone Solution. Preliminary experiments showed that hydroquinone very rapidly reduces $[RuCl_6]^{2-}$ at room temperature [9]. Reduction proceeds stoichiometrically according to the equation

$$2Na_2RuCl_6 + C_6H_4(OH)_2 + H_2O = 2Na_2Ru(H_2O)Cl_5 + C_6H_4O_2 + 2HCl.$$

Amperometric titration was carried out on the basis of the cathode current of quadrivalent ruthenium at a potential of +0.5 v (relative to the saturated calomel electrode). At this potential the hydroquinone does not give a reduction wave, and the titration curves are of the shape shown in Fig. 3. The break at the end point is very clear. Preparation of solutions for amperometric titration reduces to preparing solutions of Na_2RuCl_6, and is exactly the same as the preparation of the solutions used for taking polarograms. As titration proceeds the color of the solution lightens, and at the end point, depending on the ruthenium concentration, the solution becomes colorless, or acquires a slight rosy shade. The method can be used for 0.02-2.0 mg of ruthenium (Table 1).

The relative error for the determination of tenths and hundredths of a milligram is 1-5%. The mean reproducibility of the results, including preparation of the solutions, is 2.5%. Titration of more than 2 mg of ruthenium is complicated for the same reason as that outlined for polarographic determination of ruthenium.

Platinum, palladium, rhodium, osmium, copper, nickel, selenium, and tellurium do not interfere with the amperometric titration of ruthenium. When gold is present, the current at the end point is greater than zero; nevertheless, the break on the titration curve at the end point is still quite distinct when the amount of gold present is 20 times that of ruthenium. $[AuCl_4]^-$ ions are only slowly reduced at room temperature by hydroquinone, so that ruthenium can be determined in the presence of 15-20 times its amount of gold. Trivalent iron does not interfere with the titration as long as the amount of it present is not more than 5-10 times that of ruthenium. All the divalent iron must, however, be oxidized. Iridium interferes.

Sulfur dioxide and chlorine interfere with the amperometric titration of ruthenium for the same reasons as they interfere with its polarographic determination; the methods used for eliminating such interference are the same as those described above.

Amperometric titration of ruthenium has some advantages over its polarographic determination; the experimental conditions do not have to be observed so rigidly (temperature, rotational rate of the electrode, and the parameters of the latter), and there is no need to prepare a standard solution at the same time as the test solution, or to construct a calibration curve.

We have used the amperometric method for the determination of ruthenium in some industrial products. The results obtained are in satisfactory agreement with those obtained by gravimetric, photometric, and potentiometric methods (Table 2).

SUMMARY

A method has been developed for the polarographic determination of ruthenium on the basis of the reduction wave of $[RuCl_6]^{2-}$ on a platinum electrode. The method can be used for the determination of 1 to 200 μg Ru/ml in the presence of platinum, palladium, rhodium, osmium, and some base metals.

A method has been developed for the amperometric titration of Na_2RuCl_6 with hydroquinone solutions, using a rotating platinum electrode. The method is suitable for the determination of the same amounts of ruthenium determined by the polarographic method, but it is simpler to carry out than the polarographic method.

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DETERMINATION OF WATER IN COMPOUNDS BY THE HYDRIDE METHOD

G. M. Toptygina

N. S. Kurnakov Institute of General and Inorganic Chemistry,
Academy of Sciences, USSR, Moscow

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The hydride method suggested by Elitsur [1], in which pyridine is used as the medium, is often used for the determination of water in aquocomplex compounds. Essentially, the method depends on the fact that the pyridine, which is in contact with the test compound, removes the water from it and forms a thermally stable hydrate $C_5H_5N \times H_2O$; the latter is then decomposed with calcium hydride with the liberation of a definite amount of hydrogen ($CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$). The method has been checked on various compounds and only a few exceptions have been found in which incorrect results were obtained. These exceptions include very stable crystallohydrates (e. g., $BeSO_4 \cdot 4H_2O$) which do not give up their water completely under the experimental conditions used (water bath temperature), and also compounds which are readily reduced with liberation of gaseous products. Thus, only one reason has been advanced for explaining cases were high results have been obtained—reduction of the test compounds in contact with pyridine and calcium hydride.

According to the technique suggested by Elitsur, the pyridine is finally dehydrated prior to its use by heating a mixture of pyridine and calcium hydride in the reaction vessel on a water bath; after cooling, an aliquot of the test material is then introduced into the vessel. As the result of the interaction of water with calcium hydride, both during preliminary dehydration of pyridine and during the actual determination, a large amount of calcium hydroxide is formed, and this is a strong base whose effect on the test preparations cannot be ignored.

In order to define more closely the limits of the applicability of the hydride method of determining water, we have studied the interaction of mixtures of pyridine and calcium hydride (and calcium hydroxide) with the compounds of the elements of some of the groups in the Periodic System, in particular, with elements which possess amphoteric properties.

EXPERIMENTAL

The simple and complex chlorides of the elements were chosen mainly for our studies.

The anhydrous chlorides of aluminum, iron, zirconium, and tantalum were prepared by chlorination of the corresponding metals with gaseous chlorine; they were stored in sealed vessels in a desiccator over phosphorus pentoxide. Ammonium sulfate and chloride, chemically pure grade, were given a preliminary drying at 200-250°, while zirconium chloride hexahydrate was obtained by keeping the chemically pure octahydrate in a desiccator over sulfuric acid sp. gr. 1.84, until it had reached constant weight. The preparation of the hexachlorotitanates and chlorooxytitanates of the aklai metals and ammonia, as well as the preparation of titanium trichloride hexahydrate have been described previously [2, 3].

Pyridine was completely dehydrated as follows. Technical pyridine was distilled over calcium hydride; subsequently, the pyridine was kept in contact with calcium hydride for several months, and then redistilled over calcium hydride. The calcium hydride, pure grade, (containing calcium hydroxide as impurity) used for de-

Compound	Aliquot, g	No. of moles H_2 per mole of compound	Water content, % wt.	
			theoretical content	calc. on basis of H_2 liberated
NH_4Cl	0,0811	0,5	0	16,78
$(NH_4)_2SO_4$	0,2122	1	0	13,74
$AlCl_3$	0,0329	1	0	13,35
Cs_2TiCl_6	0,1340	2	0	6,86
$(NH_4)_2TiCl_6$	0,0951	3	0	18,39
$Cs_2TiOCl_4 \cdot H_2O$	0,1225	2	3,68	7,33
$Rb_2TiOCl_4 \cdot H_2O$	0,1155	2	4,56	9,07
$3NH_4Cl \cdot 2TiOCl_2 \cdot 4H_2O$	0,1400	7,5	14,35	27,92
$ZrCl_4$	0,1294	1,25	0	9,62
$ZrOCl_2 \cdot 6H_2O$	0,3760	5,66	37,74	35,6
$TiO_2 \cdot nH_2O$	0,5309	0,26	13,10*	5,11
$TiCl_3 \cdot 6H_2O$	0,0597	6	41,19	41,07
$TaCl_5$	0,2503	2	0	9,75
$FeCl_3$	0,1536	1	0	11,93

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* Water was determined by loss in weight on calcining.

composing traces of calcium nitride with the traces of moisture in the pyridine, was heated with pyridine on a water bath in the apparatus which was subsequently used for water determination. No calcium hydroxide was added, since we observed that it always appeared in the reaction mixture during preliminary dehydration of pyridine.

The technique used has been described in detail in Elitsur's article [1].

As the results in the table show, of all the compounds tested, only titanium trichloride hexahydrate contained the amount of water, calculated on the basis of the amount of hydrogen liberated, which was equal to the theoretical value. A certain amount of hydrogen was liberated even during the interaction of the anhydrous chlorides of titanium, zirconium, tantalum, iron, aluminum, and ammonia with a mixture of pyridine, calcium hydride, and calcium hydroxide.

The explanation for this lies in the fact that all the compounds listed interact with the calcium hydroxide in the reaction mixture, as a result of which the hydroxides of the respective metals are formed. Formation of hydroxides were observed in some cases experimentally; amorphous flocculent precipitates appeared in the mixture, and sometimes these floated to the surface. This process was very rapid in those cases where the chloride dissolved in pyridine (e. g. $TiCl_3$, $ZrCl_4$) and optimum conditions were obtained for contact with the calcium hydroxide. In the case of insoluble compounds (e. g. NH_4Cl, $(NH_4)_2SO_4$), the reaction process was speeded up by stirring the reaction mixture. Of course, compounds of group I and II elements do not react with calcium hydroxide and do not give high water contents during their determination.

The hydroxides formed are distinguished by differences in the stability of the water bond; this stability can be characterized by the temperature at which the water is split off on heating. Ammonium hydroxide is an unstable compound and immediately it is formed it gives up water to the pyridine; the hydrate of the latter interacts with calcium hydride to liberate hydrogen at the rate of 0.5 mole per 1 g · ion of ammonia, and this was actually observed in practice:

$$\begin{array}{c} 4NH_4Cl+2Ca(OH)_2=2CaCl_2+4NH_3+2H_2O \\ 2H_2O+CaH_2=Ca(OH)_2+2H_2 \\ \hline 4NH_4Cl+Ca(OH)_2+CaH_2=2CaCl_2+4NH_3+2H_2 \end{array}$$

The hydroxides of the elements tested can be divided into two groups: the elements of one group give up all their water under reaction conditions and give oxides, apparently, as the final product; the elements of the other group give up only a part of their water.

According to our results, one mole of the anhydrous chlorides of aluminum and iron liberated one mole of hydrogen during the reaction; the reactions which occur can be expressed by the following equations:

$$\begin{array}{c} 2Me^{III}Cl_3+3Ca(OH)_2=3CaCl_2+2Me^{III}(OH)_3 \\ 2Me^{III}(OH)_3+2CaH_2=2Ca(OH)_2+2Me^{III}O(OH)+2H_2 \\ \hline 2Me^{III}Cl_3+Ca(OH)_2+2CaH_2=3CaCl_2+2Me^{III}O(OH)+2H_2 \end{array}$$

These results agree with published data* on aluminum hydroxide. During the interaction of aluminum salts with alkali, the ortho hydrated oxide $Al(OH)_3$ is formed, which splits off part of the water and is converted into the considerably more stable meta-form of the hydroxide AlO(OH). AlO(OH) is formed at temperatures below 170°.

By analogy, tantalum hydroxide presumably splits off two molecules of water, since two moles of hydrogen are formed per mole of $TaCl_5$ during the reaction.

In the case of zirconium compounds, the number of moles of H_2 split off per mole of the compounds is a fraction. Forms with a definite composition are not known for zirconium hydroxides. Dehydration of the hydroxides starts at a low temperature and proceeds gradually with increasing temperature. Some water, 0.75 mole per mole of ZrO_2, remains in the hydroxide at a temperature of about 120° [4].

During determination of water in quadrivalent titanium compounds, we established that one mole of $TiCl_4$ splits off an additional two moles of hydrogen, while one mole of $TiOCl_2$ splits off one mole of H_2. According to these results, the reactions proceed as follows:

$$\begin{array}{c} TiCl_4+2Ca(OH)_2=Ti(OH)_4+2CaCl_2 \\ Ti(OH)_4+CaH_2=TiO_2+Ca(OH)_2+2H_2 \\ \hline TiCl_4+Ca(OH)_2+CaH_2=TiO_2+2CaCl_2+2H_2 \end{array}$$

$$\begin{array}{c} 2TiOCl_2+2Ca(OH)_2=2TiO(OH)_2+2CaCl_2 \\ 2TiO(OH)_2+CaH_2=2TiO_2+Ca(OH)_2+2H_2 \\ \hline 2TiOCl_2+Ca(OH)_2+CaH_2=2TiO_2+2CaCl_2+2H_2 \end{array}$$

Nevertheless, thermal analysis which we carried out on titanium hydroxides, precipitated both hydrolytically from solution, and by ammonia, showed that a large fraction of the water is split off at 120°, but not all the water. All the water in the hydroxide is not determined by Elitsur's method either. It is possible that this deviation can be explained by the fact that pyridine reacts with titanium hydroxide at the moment it is formed, and its properties may differ from those of the gell of titanic acid dried over a long period.

Trivalent titanium hydroxide, under conditions which exclude oxidation, is a stable compound, and, presumably, holds the water of constitution more firmly than does pyridine; accordingly liberation of six moles of hydrogen per mole of titanium trichloride hexahydrate is observed, in agreement with the known water content.

On the basis of our results and those of Elitsur, the following conclusions can be drawn.

When a simple or complex compound does not decompose in a pyridine medium, then the amount of constitutional water will be determined by the hydride–pyridine method, as long as the temperature at which the compound splits off water does not exceed about 170°. It should be noted that many compounds, e. g., $TiCl_3 \cdot 6H_2O$, and the chlorooxytitanates of the alkali metals, are decomposed by pyridine, and thereby liberate water which reacts with the calcium hydride.

When the compound of any element interacts with the calcium hydroxide present in the reaction mixture, then correct determination of water in the compound depends on the bond stability of the constitutional water in the hydroxide of this element; the water which is split off from the hydroxide at temperatures below 150-170° will react with calcium hydride. Most of the compounds of many of the elements in III, IV, V and the subsequent groups of the Periodic System will, presumably, belong to this group.

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* The data on the hydroxides were taken from "Gmelins Handbuch der Anorganischen Chemie"; no reference to the source was given in the handbook.

SUMMARY

The range over which the hydride method with pyridine can be used is very limited. Compounds of aluminum, iron, lanthanum, and cerium which, according to the results given in Elitsur's article, give correct values for their water content, should give high values for water, since the hydroxides of lanthanum, cerium, and other rare earth elements split off part of their water at temperatures below 150° [5].

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ANALYSIS OF THE BORIDES OF THE TRANSITIONAL AND RARE EARTH ELEMENTS

L. N. Kugai and T. N. Nazarchuk

Institute of Metalloceramics and Special Alloys,
Academy of Sciences, Ukr. SSR, Kiev

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Amorphous boron can be oxidized to boric acid by potassium permanganate [1], ceric sulfate [2], a mixture of hydrogen peroxide and nitric acid [3], and also by potassium iodate and periodate [4]. A method which has been developed for the determination of free boron in boron carbide [5] is based on the difference in the oxidizability of free boron and of boron combined as the carbide.

In the work described here we studied the behavior of the borides of the transitional elements: TiB_2, ZrB_2, CrB_2, W_2B_5 and the hexaborides of the rare earths: Y, La, Ce, Pr, Nd, Sm, Gd towards various oxidizing mixtures capable of oxidizing amorphous boron: a nitric acid – hydrogen peroxide mixture, a sulfuric acid solution of potassium iodate, and a sulfuric acid solution of ceric sulfate. It was thought that it might be possible, on the basis of differences in the stability of free boron and of the borides listed above to the oxidizing mixtures mentioned, to develop a technique for determining free boron in these borides.

The Stability of the Borides in Solutions of Hydrogen Peroxide and Nitric Acid. An aliquot of the finely ground boride (270 mesh) was treated with the reagent in a flask made of boron-free glass, and fitted with a ground glass reflux condenser. When the aliquot was not decomposed completely, the insoluble residue was filtered off on a glass filter, thoroughly washed with water, dried to constant weight, and weighed. An aliquot of this dried residue was taken for repeated treatment with the oxidizing mixture. The boron and metal contents of the filtrate were determined.

Borides with the chemical composition given in Table 1 were used in the work.

During a study of the stability of the borides in solutions consisting of mixtures of hydrogen peroxide and nitric acid, it was observed that zirconium diboride was the most stable compound toward this oxidizing mixture. The remainder of the borides listed above were either decomposed completely by the mixture (YB_6, LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, GdB_6), or partially (CrB_2, TiB_2, W_2B_5) decomposed within the time indicated.

In view of these findings, only the oxidation of ZrB_2 by the hydrogen peroxide – nitric acid mixture was studied in detail.

As the results in Table 2 show, the same amount of boron dissolved, independently of the time for which the boride was treated, and of the hydrogen peroxide concentration.

The residue obtained after the first treatment with the hydrogen peroxide – nitric acid mixture was treated a second time with the same mixture over a similar time period. It was established that during the second treatment of zirconium boride with the oxidizing mixture no boron dissolved. These results indicate that it should be possible to determine free boron in zirconium boride.

In order to check on the method suggested, a series of determinations of free boron in synthetic mixtures of ZrB_2 and amorphous boron was carried out. The results obtained are given in Table 3.

TABLE 1

Chemical Composition of the Borides

Transitional metal borides				Rare earth hexaborides			
boride	content, %			boride	content, %		
	metal	B	C_{formed}		metal	B	C_{formed}
ZrB_2	82,0	18,0	—	YB_6	59,4	40,6	—
	82,9	16,0	—				
CrB_2	69,7	28,9	0,4	LaB_6	69,35	30,60	—
TiB_2	69,05	30,0	0,35	CeB_6	68,8	27,7	0,13
W_2B_5	88,0	11,30	0,3	PrB_6	70,1	30,1	—
				NdB_6	70,9	27,65	—
				SmB_6	71,20	27,5	0,2
				GdB_6	71,9	28,2	—

TABLE 2

Primary Treatment of ZrB_2 with Hydrogen Peroxide – Nitric Acid

Sample No.	Mixture of 20 ml hydrogen peroxide (1 : 3) and 10 drops HNO_3					Mixture of 20 ml hydrogen peroxide (1 : 2) and 10 drops HNO_3				
	sample wt g	time of treatment	0.1 N NaOH ml	0.1 N NaOH in the blank, ml	% Boron (free)	sample wt., g	time of treatment	0.1 N NaOH ml	0.1 N NaOH in the blank, ml	% Boron (free)
I	1,0	30	1,15	0,3	0,090	1,0	30	1,20	0,4	0,085
	1,0	45	1,20	0,3	0,097	1,0	45	1,20	0,4	0,085
	1,0	60	1,10	0,25	0,085	1,0	60	1,25	0,4	0,090
	0,5	30	0,70	0,3	0,085					
	0,5	45	0,70	0,25	0,090					
II	1,0	30	0,30	0,25	Free boron absent	1,0	30	0,35	0,40	Free boron absent
	1,0	45	0,30	0,30		1,0	45	0,35	0,35	
	1,0	60	0,30	0,25		1,0	60	0,40	0,40	
	0,5	30	0,30	0,30						

TABLE 3

Determination of Free Boron in Synthetic Mixtures Containing Amorphous Boron (Weight of ZrB_2 taken was 0.5 g. Dissolution was carried out in hydrogen peroxide (1 : 3) and 10 drops of HNO_3)

Boron added, mg	8,30	14,90	20,60	23,10	30,30	43,00	49,0	51,0
Boron found, mg	8,48	14,97	20,29	22,81	29,87	42,46	48,90	50,75
Relative error, %	+2,16	+0,47	−1,5	−1,25	−1,41	−1,25	−0,2	−0,5

It is clear from these results that the free boron content of zirconium boride can be determined with reasonable accuracy by the method suggested.

Analytical Procedure. A 1-g aliquot of zirconium boride is dissolved on heating for 30-40 min in 20 ml of hydrogen peroxide (1 : 3) and ten drops of nitric acid, contained in a flask fitted with a reflux condenser. The residue is filtered off. The filtrate is neutralized, first by 10% NaOH solution free from carbonate, and then with

TABLE 4

The Solubility of the Borides of the Rare Earths and Thorium in Acids and Mixtures of Acids

Boride	HNO_3 (1:1)	Aqua regia (1:1)	H_2SO_4 1:1 +5 drops of HNO_3	HCl (1:1)	H_2SO_4 (1:1)
YB_6	Complete dissolution on gentle heating for 5 min.	Complete dissolution in the cold or on gentle heating for 5 min.	Complete dissolution on gentle heating for 5 min.	77—78%	71—72%
LaB_6				93—94%	89—92%
CeB_6				84—86%	83—84%
PrB_6				90—94%	27—30%
NdB_6				87—88%	78%
SmB_6				79—80%	77%
GdB_6				91—93%	87%
ThB_6				82%	

0.1 N or 0.01 N NaOH to the methyl red end point. Ten ml of a neutral solution of inert sugar or 1 g of mannitol is added, and the boric acid titrated to the phenolphthalein end point with 0.1 N or 0.01 N sodium hydroxide.

Stability of the Borides in Acid Solutions of Potassium Iodate and Ceric Sulfate. The diborides of chromium, titanium, and zirconium, as well as boron nitride and carbide, do not dissolve either in the cold, or on heating, in acid solutions of potassium iodate and periodate [4]. Elemental boron readily dissolves in these solutions, and use has been made of this fact for the determination of boron in elemental boron and in borides (MgB_2, MgB_6, MgB_{12}, CaB_6, BaB_6) [4].

We wanted to use sulfuric acid solutions of potassium iodate and periodate for determining free boron in chromium, titanium, and zirconium diborides and in rare earth elements hexaborides. The experiments which we carried out showed that the borides TiB_2, ZrB_2, CrB_2 and the hexaborides of Y, La, Ce, Nd, Sm, Gd react with a sulfuric acid solution of potassium to liberate iodine. The borides which we tested also proved unstable in acid solutions of ceric sulfate. Consequently, acid solutions of ceric sulfate and potassium iodate could not be used for the determination of free boron in borides.

Acid Stability, Alkali Stability, and Analytical Methods for the Hexaborides of the Rare Earths. The dissolution of the hexaborides of Y, La, Ce, Pr, Nd, Sm, Gd in hydrochloric, nitric, and sulfuric acids and in mixtures of these acids was studied, as well as their dissolution in aqueous alkali solutions. Platinum vessels were used for dissolution of the hexaborides in alkalis.

Results obtained on the solubility of the hexaborides in acids are given in Table 4.

The amount of insoluble residue (%) remaining after treating the borides with acids for two hours is given in the last two columns of this table.

It follows from these results that the rare earth hexaborides listed above are comparatively readily decomposed by acids. In order of their stability in hydrochloric acid,they can be arranged in the following series: LaB_6, PrB_6, GdB_6, NdB_6, CeB_6, SmB_6, YB_6; while in sulfuric acid this order is LaB_6, GdB_6, CeB_6, NdB_6, SmB_6, YB_6, PrB_6.

The rare earth hexaborides hardly dissolve at all in aqueous alkali solutions. The exception is CeB_6 which is decomposed by a mixture of sodium hydroxide and hydrogen peroxide.

Analytical Procedure for the Rare Earth Hexaborides. The hexaboride (0.5 g)(Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Yb, Th) is dissolved on gentle heating in 20 ml of nitric acid (1 : 1) contained in a flask fitted with a reflux condenser. The solution obtained is transferred to a 250 ml standard flask and its volume made up to the mark with water. The rare earth and thorium content is determined by titration with sodium ethylenediaminetetracetate (EDTA-Na) using arsenazo as indicator [6], or gravimetrically by the oxalate method. An aliquot (50 ml) of the solution is transferred to a 350 ml conical flask, 3-5 drops of pyridine is added, and ammonia added to adjust the pH to 6-7, using universal indicator paper; 2-3 drops of a 0.5% aqueous solution of arsenazo is added and the rare earths titrated with 0.025 M EDTA-Na until the color of the solution changes from violet to yellow-rose. Thorium is titrated at pH 2-4. The EDTA-Na solution is standardized against lanthanum nitrate solution of known concentration.

Boron Determination. For determination of boron in the rare earth borides (with the exception of SmB_6) a method is suggested which does not involve preliminary removal of the rare earth element. The rare earth element is complexed by addition of EDTA-Na, and boron determined by the usual titrimetric method. The exact amount of EDTA-Na must be added to complex the rare earth element. This amount has already been determined during titration of the rare earth element. An aliquot (50 ml) of the solution is transferred to a 300 ml conical flask, and the exact amount of 0.025 M EDTA-Na solution added from a buret. The solution obtained is neutralized with sodium hydroxide using methyl red as the indicator, and boron then determined as usual by titrating it with 0.1 N NaOH using phenolphthalein as the indicator in the presence of mannitol or invert sugar.

The method suggested has been checked by comparing it with the normal method of determining boron, in which the rare earths are removed by precipitation with $BaCO_3$. Satisfactory results were obtained. For determination of boron in the borides of Sm and Th, Sm and Th must be removed by precipitating them with barium carbonate.

SUMMARY

A technique has been developed for the determination of free boron in zirconium boride; it is based on the difference between the oxidizability of free boron and of combined boron with a mixture of hydrogen peroxide and nitric acid.

It has been shown that acid solutions of ceric sulfate and potassium iodate cannot be used for the determination of boron in the borides of Ti, Zr, Cr, W, and the rare earth elements, since the borides themselves are soluble to a considerable extent in these mixtures.

A simple method is suggested for the analysis of the rare earth hexaborides.

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QUANTITATIVE DETERMINATION OF TRACES OF BARIUM, NICKEL, COPPER, ANTIMONY, MOLYBDENUM, MANGANESE, CADMIUM, TIN, GOLD, AND ARSENIC IN METALLIC BERYLLIUM BY A RADIOACTIVATION METHOD

V. R. Negina and V. N. Zamyatnina

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A radioactivation method has been used for the determination of lithium, nitrogen, fluorine, aluminum, and vanadium present as impurities in metallic beryllium [1]. Work has also been published on the determination of total rare earths [2] and oxygen [3, 5] in beryllium. In the work described here the content of Ba, Ni, Cu, Sb, Mo, Mn, Cd, Sn, Au, As present as impurities in metallic beryllium has been determined on the basis of the activity of the products formed as the result of the capture of thermal neutrons (Ba^{139}, Ni^{65}, Cu^{64}, Mn^{56}, Sb^{122}, Mo^{99}, Cd^{115}, Sn^{121}, Au^{198}, As^{76}).

The basic characteristics of the isotopes used are given in Table 1.

The sensitivity of the determination is calculated for a stream of 0.5×10^{12} neutrons/cm^2, and irradiation time of three hours for 40 decays/sec towards the end of irradiation. The actual sensitivity of the determination is always below the calculated value, since during the time elapsing between the end of irradiation and the beginning of activity measurements, the activity of the element decreases with its half-life period. In addition, not all the activity obtained toward the end of irradiation is measured, because of the loss which occurs during chemical separation and purification.

A relative method was used for determining the content of impurities. The test beryllium samples (1 g) were placed in polyethylene cassettes, which together with standards, were placed in a polyethylene container. Under the irradiation conditions chosen, activation of the polyethylene is insignificant. Irradiation of the test samples and standards was carried out in a homogeneous stream of thermal neutrons. After irradiation, the radioactive isotopes were isolated on isotopic carriers (20-30 mg calculated as the metal for each element). Since there was only a limited amount of test material, the test elements were divided into two groups: Ba, Ni, Cu, Sb, Mo and Mn, Cd, As, Au, Sn. Methods were developed for separating these elements from beryllium and for their radiochemical purification. The basis of the method was extraction of the diethyldithiocarbamate complexes of the test elements in chloroform [4], during which barium and beryllium remain in solution.

Separation of Mn^{II}, Cd, Au, As, Sn^{IV} from Irradiated Beryllium, Their Separation, and Purification. Concentrated hydrochloric acid, Mn^{II}, Au, Cd, As, Sn^{IV} carriers, and the irradiated metallic beryllium were placed in an apparatus provided with a reflux condenser.

After the samples had dissolved, the diethyldithiocarbamate complexes of As, Au, Sn^{IV} were extracted from the solutions in 10-12 N HCl with chloroform. Mn^{II} and Cd were extracted with chloroform from 1 N HCl; these elements were then reextracted into dilute (1 : 3) nitric acid, after which cadmium disulfide and manganese dioxide were precipitated.

In order to separate As, Au, and Sn^{IV}, the chloroform extract was evaporated to dryness and the residue boiled with nitric acid. The dry residue was dissolved in concentrated hydrochloric acid and gold and arsenic

TABLE 1

Test micro-impurity	Original isotopes	Activation cross section for thermal neutrons, 10^{-24} cm^2	Distribution of the isotope, %	Reaction product	Half-life period	Calculated sensitivity of the determination of the impurity, g
Mn	Mn^{55}	12,7	100	Mn^{56}	2,7 Hr.	$0,9 \cdot 10^{-9}$
Cd	Cd^{114}	0,28	10	Cd^{115}	56 Hr.	$1,25 \cdot 10^{-6}$
As	As^{75}	4,2	100	As^{76}	26 Hr.	$2,5 \cdot 10^{-8}$
Au	Au^{197}	96	100	Au^{198}	65 Hr.	$8,6 \cdot 10^{-8}$
Sn	Sn^{120}	0,14	32	Sn^{121}	28 Hr.	$4,9 \cdot 10^{-7}$
Ba	Ba^{138}	0,5	71	Ba^{139}	84 Min.	$9,1 \cdot 10^{-8}$
Ni	Ni^{64}	2,6	1	Ni^{65}	2,6 Hr.	$6 \cdot 10^{-7}$
Cu	Cu^{63}	3,9	69	Cu^{64}	12,8 Hr.	$4 \cdot 10^{-8}$
Sb	Sb^{121}	6,8	57	Sb^{122}	2,8 Min.	$1,35 \cdot 10^{-7}$
Mo	Mo^{98}	0,13	23	Mo^{99}	67 Hr.	$1,2 \cdot 10^{-6}$

sulfides precipitated with hydrogen sulfide. Tin was isolated as its sulfide from a solution which was 1 N with respect to hydrochloric acid.

The gold and arsenic sulfides were dissolved in concentrated HCl containing hydrogen peroxide. Gold was extracted from a solution 1 N with respect to hydrochloric acid by means of diethyl ether. After removal of the gold, the aqueous layer was acidified to 6-8 N HCl and the arsenic reduced with hypophosphite to its elemental form.

In order to obtain radiochemically pure preparations, in addition to the separation operations, tin was purified further by precipitation of cesium hexachlorostannate from 12 N hydrochloric acid in the presence of hydrogen peroxide, and by precipitation as tin sulfide from a weakly acid medium; cadmium was purified further by precipitation of ferric hydroxide with pure ammonia, precipitation of cadmium sulfide from a weakly acid medium, and precipitation of the double phosphate of cadmium and ammonia; arsenic was purified further by precipitation as magnesium and ammonium arsenate; while manganese was purified by precipitation of manganese and ammonium phosphate. Gold was purified from radioactive contamination during its separation without additional chemical operations.

Isolation of Ba, Ni, Cu, Sb, and Mo from Irradiated Beryllium Their Separation, and Purification. Of the isotopes isolated, the ones with the shortest half-life period were Ba^{139} (T = 85 min) and Ni^{65} (T = 2.7 hr). Accordingly, in the method used, provision was made for separating these metals first.

Into an apparatus (fitted with a reflux condenser) containing 10-12 N hydrochloric acid were placed nickel, copper, antimony, and molybdenum carriers, and the irradiated metallic beryllium. The solution obtained was diluted until it was 3 N with respect to hydrochloric acid, barium was then added, and isolated as its sulfate.

Prior to extraction of the diethyldithiocarbamate complexes of Ni, Cu, Sb, and Mn from 3 N HCl, into chloroform, the antimony was reduced with hydrazine hydrochloride. After extraction, the chloroform extract containing nickel, copper, antimony, and molybdenum was evaporated to dryness and boiled with concentrated nitric acid. The dry residue was dissolved in 4% ammonia. Nickel, copper, and molybdenum dissolved, while antimony remained in the residue.

Nickel was isolated by extracting it as its dimethylglyoxime complex into chloroform from a weakly ammoniacal medium.

Nickel was reextracted from the chloroform into 2 N hydrochloric acid, and was reprecipitated as nickel dimethylglyoximate.

Copper was isolated by adding hydrochloric acid to the solution to give a neutral reaction, and extracted as copper dimethylglyoximate with chloroform. Copper was reextracted from the chloroform into ammonia, and was reprecipitated as cupric hydroxide. Molybdenum was isolated as its sulfide from a weakly acid medium.

The residue remaining after dissolving the dry residue in 4% ammonia was dissolved in 12 N HCl, and antimony sulfide precipitated from a solution 2 N with respect to hydrochloric acid. Since the antimony sulfide

TABLE 2

Test element	Av. content of the impurity in 1g of metallic beryllium, g	Average value of the impurity content, %	Relative experimental error, %
Cu	$3{,}7 \cdot 10^{-5}$	$3{,}7 \cdot 10^{-3}$	± 8
Ni	$5 \cdot 10^{-5}$	$5 \cdot 10^{-3}$	± 6
Sb	$3 \cdot 10^{-8}$	$3 \cdot 10^{-6}$	±10
Mo	$1{,}23 \cdot 10^{-5}$	$1{,}23 \cdot 10^{-3}$	±10
Ba	$2 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	+ 4
Mn	$4 \cdot 10^{-7}$	$4 \cdot 10^{-5}$	±10
Cd	$2{,}8 \cdot 10^{-6}$	$2{,}8 \cdot 10^{-4}$	± 3
Sn	$5{,}3 \cdot 10^{-5}$	$5{,}3 \cdot 10^{-3}$	±10
Au	$3{,}7 \cdot 10^{-8}$	$3{,}7 \cdot 10^{-6}$	±47**
As	$2{,}7 \cdot 10^{-7}$	$2{,}7 \cdot 10^{-5}$	± 6

precipitate contained traces of molybdenum, while the molybdenum precipitate contained traces of antimony, to separate these elements from each other, the precipitates were combined and washed with hot 6 N HCl. The antimony dissolved while the molybdenum remained in the precipitate. Antimony sulfide was precipitated from a weakly acid medium with hydrogen sulfide.

For obtaining radiochemically pure preparations, the following additional purification operations were used: for purifying barium, its sulfate was fused with a mixture of soda and potassium carbonate and after leaching with water, barium carbonate was precipitated; it was then precipitated with ferric hydroxide using pure ammonia, and finally precipitated as barium chromate; antimony was purified by extraction as quinquevalent antimony from 12 N hydrochloric acid with isopropyl ether, and precipitation as antimony sulfide from 2 N HCl after removal of the ether and precipitation as metaantimonic acid; molybdenum was purified by extracting it from 5 N hydrochloric acid in the presence of hydrazine hydrochloride, with subsequent reextraction into water and precipitation as molybdenum sulfide. Nickel and copper were purified from radioactive contamination without additional chemical purification. The standards of the test elements were purified from radioactive contamination in the same way as the test samples.

Target Measurement and Treatment of Results. The test element and its standard were placed on the targets used for measurement in the same gravimetric form. The amount of material on the targets and the measurement conditions were standardized, so that there was no need for applying corrections for self-absorption and self-scattering.

A MST-17 torsion counter in a B-2 setup was used for measuring the activity. In order to check on the radioactive purity of the elements isolated, decay curves were taken, and, when it was possible, absorption curves in aluminum were also taken. Identification of the preparations isolated showed that the techniques adopted enable one to obtain the test elements with the requisite radioactive purity.

After the activity measurements, the exact amount of material placed on the target was determined, after drying it or after ignition under definite conditions. For this purpose, gold sulfide was calcined at a temperature of 600° to the metal, while tin sulfide was converted into its dioxide at 600°; the magnesium and ammonium arsenate compound, the double phosphate of manganese and ammonium, and the double phosphate of cadmium and ammonium were calcined at 800° to give the compounds $Mg_2As_2O_7$, $Mn_2P_2O_7$, $Cd_2P_2O_7$.

Barium chromate was brought to constant weight at 600°, while nickel dimethylglyoximate and cupric hydroxide were ignited at 800° to give the oxides NiO and CuO. Molybdenum sulfide was calcined at 500° to MoO_2, and the precipitate of metaantimonic acid to Sb_2O_4 at 800°. Quantitative yields of the elements after separation and purification amounted to 60-80 %.

The activity of the elements in samples of the test material and in a standard sample at a definite time were found from the activity measurements.

The amount of an impurity in a test sample (X) was determined by means of the formula

$$X = \frac{Bma}{A_e M} \cdot \frac{A_x}{b},$$

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* The error was calculated either by the mean square method, or mean statistical, depending on the number of samples analyzed.

** The comparatively large relative error is the result of uneven distribution of gold as an impurity in the test samples where A_e is the activity of the element in the standard target referred to a definite time, A_x is the activity of the element in a target of the test sample referred to the same time, M is the amount of carrier added to the standard sample, B is the amount of carrier added to the test sample, a is the weight of sample in the standard target, b is the weight of material in a target with test sample, and m is the amount of material in the standard sample.

The formula was derived on the assumption that the impurity content (X) and the amount of material in test samples (m) is negligibly small compared with the amounts of carriers introduced M and B.

Results of the analysis of metallic beryllium for its content of Ba, Ni, Cu, Sb, Mo, Mn, Cd, As, Au, Sn present as impurities are given in Table 2.

The amount of gold and antimony present as impurities in one gram of metallic beryllium was lower than the calculated sensitivity of determination, by 2.3 times in the case of gold and 4.5 times in the case of antimony. As a result, the activity of antimony and gold targets, as a rule, did not exceed 50-100 impulses per minute against the background at the beginning of activity measurements.

So that the small number of impulses measured did not affect the accuracy of the determination of gold and antimony, the time for which the targets were measured was increased so that the statistical count error did not exceed 3%.

L. S. Chikisheva, M. A. Presnyakova, E. Shamonina, and P. P. Shevchenko took part in the work.

SUMMARY

Methods have been developed for the separation of beryllium, barium, nickel, copper, antimony, molybdenum, manganese, cadmium, gold, tin, and arsenic. It has been established that As, Au, Sn^{IV}, Ni, Cu, Sb^{III}, Mo can be extracted as their diethyldithiocarbamate complexes from 10-12 N HCl with chloroform. It has been found that in order to extract the diethyldithiocarbamate complex of antimony completely into the chloroform, the antimony must be reduced beforehand with hydrazine hydrochloride.

A radioactivation method has been developed for the determination of Ba, Ni, Cu, Sb, Mo, Mn, Cd, Sn, Au, and As present as impurities in metallic beryllium.

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RADIOACTIVATION DETERMINATION OF IMPURITIES IN HIGH PURITY THALLIUM

I. P. Alimarin, Yu. V. Yakovlev, M. N. Shchulepnikov,
D. A. Vlasov, G. M. Chernov, and Yu. A. Surkov

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Increasing the sensitivity of the determination of impurities in semiconducting materials is one of the most important problems of analytical chemistry. One of the highly sensitive methods of analysis which has been successfully used for the analysis of semiconductors both in the USSR and abroad, is radioactivation analysis [1-6]. The method consists essentially or irradiating the test material with a stream of slow neutrons, the interaction of which with microamounts of impurities leads to the formation of the corresponding radioisotopes; their activity is proportional to the mass of the test element.

Deuterons, α-particles, protons, and γ-rays are also used for the purposes of radioactivation analysis, but to a much lesser extent than neutrons. Test samples are usually irradiated in a nuclear reactor.

The use of neutron streams with an intensity of about 10^{12} - 10^{13} neutrons/cm^2/sec, and a sample weight of about 1 g, permits determination of a large number of elements with a sensitivity of 10^{-6} - 10^{-8} % [4]. For quantitative determination of the impurities, standards are used which contain known amounts of the test elements, and which are irradiated under the same conditions as those used for the samples.

The expenditure of a large amount of time in chemical separation, and the impossibility of identifying radioisotopes which have similar half-life periods without measuring the energy of their β-particles, complicate the use of the radiochemical variant of the method in a number of instances.

The use of a γ-scintillation spectrometer makes it possible to avoid these difficulties, as long as the sample, in which it is desired to determine the impurities, does not emit γ-rays, or the half-life period of the radioisotopes of the macrocomponent is so small, that by the time measurements are started, they have completely decayed. Examples of materials which can be analyzed without chemical separation, are silicon, graphite, thallium, and some other semiconducting materials.

The negligible self-absorption of γ-rays in the sample makes preparation of the samples for measurement simple.

The principle of the method consists in recording the γ-radiation emitted by the radioactive isotopes of the test elements by means of a detector, consisting of a NaI(T1) crystal (d = 30 mm, h = 20 mm) and a FÉU-S photomultiplier in a lead chamber. The collimators are located within the protective chamber. The spectrum impulses from the photomultiplier pass through a linear accelerator and discriminator into a fifty channel amplitude analyzer. The recording of the signals on the analyzer tube permits a record of the spectrum to be obtained on a linear scale. A so-called "circle–point" system is used in the memory setup. The rays of the cathode ray tube are turned round a point raster, the geometrical location of the irradiating points in the upper part of the raster is the spectrum to be measured.

The use of a γ-scintiallation spectrometer makes it possible to carry out both a qualitative determination of the impurities on the basis of one or more photo peaks, corresponding to the photoelectric absorption of the characteristic γ-rays, and a quantitative determination on the basis of the area or the height of the photo peaks, after taking into account the efficiency of the crystal for the various energies of the γ-rays, or by using standards. Additional identification is carried out by measuring the half-life period on the basis of the rate at which the value of the photo peaks falls off.

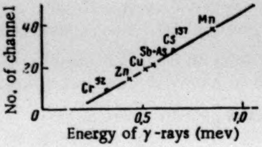

Fig. 1. Calibration curve of the spectrometer.

We have carried out some work on the determination of Mn, Zn, Cu, As, and Sb present as impurities in four samples of metallic thallium, using a fifty channel γ-scintillation spectrometer, without preliminary chemical separation. An aliquot (about 0.5 g) of a sample and the standards in the form of microamounts of the salts of the test elements, were placed in a quartz weighing bottle, preliminary treated with hot aqua regia and then washed with water, ethanol, and ether; the weighing bottles were wrapped in aluminum foil, placed in aluminum cases and irradiated with a neutron stream ($f = 0.87 \times 10^{13}$ neutrons/cm^2/sec) for 20-48 hours. After irradiation, the thallium sample was removed from the weighing bottle, pickled with concentrated hydrochloric acid, washed three times with water, ethanol, and ether; it was then transferred to a small test tube and used for measurements on a γ-spectrometer.

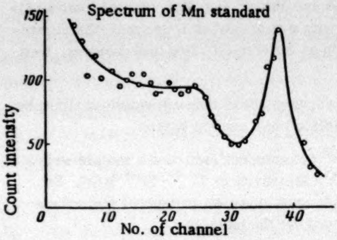

Fig. 2. Spectrum of the manganese standard.

The microamounts of the standards were washed out of the weighing bottles with 0.6 N hydrochloric acid, and carriers of the corresponding elements in amounts of 5-10 mg were added to the solution; they were then subjected to several purification operations to free them from contaminating impurities, mainly sodium.

In order to purify the manganese standard, it was precipitated with ferric hydroxide which was added to the solution containing the manganese; manganese dioxide was then precipitated twice with $KClO_3$, after which the double phosphate of ammonium and manganese was precipitated; finally, the latter, after calcining at 800° for 15 min, was weighed as manganese pyrophosphate.

The copper standard was purified by precipitating the copper as sulfide and thiocyanate. The thiocyanate precipitate was washed three times with water, ethanol, and ether, and finally dried and weighed.

The zinc standard was purified by precipitating it twice as zinc thiocyanomercuriate, which, after washing with water, ethanol, and ether, was weighed. The following purification operations were carried out on the antimony standard: precipitation as the sulfide and as metaantimonic acid. The precipitate obtained was washed with water, ethanol, and ether, it was then placed in a porcelain crucible, calcined to Sb_2O_4, and weighed.

The arsenic standard was purified by precipitation as its sulfide, followed by reduction of arsenic to the elemental state with sodium hypophosphite; the precipitate was washed three times with water, ethanol, and ether, dried and weighed.

The tared residues of the purified preparations of the standards were transferred to small test tubes and then measurements carried out on them.

An energy calibration of the analyzer scale was carried out prior to commencing measurements on the γ-spectrometer. Calibration was carried out using the radioactive isotopes Cs^{137} (E_γ = 0.66 Mev) and Cr^{52} (E_γ = = 0.32 Mev). In Fig. 1 is shown the calibration curve for the spectrometer constructed by means of Cs^{137} and Cr^{52}, the energies of the photo peaks of the Mn, Zn, Cu, As, and Sb standards are included. The spectra of the

Sample No.	Impurities determined, %				
	Mn	Cu	Zn	Sb	As
0	$2{,}9\cdot10^{-7}$	$3\cdot10^{-7}$	—	$<4\cdot10^{-6}$	$2\cdot10^{-6}$
1	$1{,}3\cdot10^{-7}$	$1\cdot10^{-7}$	$4\cdot10^{-5}$	$<9\cdot10^{-6}$	$5\cdot10^{-6}$
2	$<4.10^{-8}$	$1{,}8\cdot10^{-7}$	$1\cdot10^{-5}$	$<2\cdot10^{-6}$	$1\cdot10^{-6}$
145	$<4\cdot10^{-8}$	$<1\cdot10^{-7}$	—	$<2\cdot10^{-6}$	$1\cdot10^{-6}$

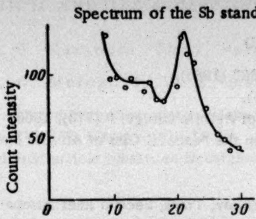

Fig. 3. Spectrum of the antimony standard

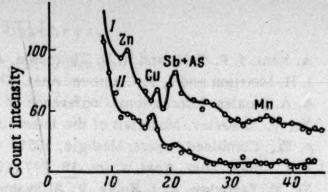

Fig. 4. Spectrum of thallium samples. I) Spectrum of sample No. 1; II) spectrum of sample No. 2.

manganese and antimony standards are shown in Figs. 2 and 3. Spectra of test samples of thallium (Nos. 1 and 2) are shown in Fig. 4. Photo peaks corresponding to Mn, Zn, Cu, and As + Sb are evident on Fig. 4. The photo peak in channel 23 could be the total photo peak of the isotopes As^{76} (E_γ = 0.56 Mev) and Sb^{122} (E_γ = 0.57 Mev). For identification purposes the decay curve of this photo peak was taken. The half-life period proved to be close to that of the period of As^{76} (T = 26 hr). Consequently, the area of the photo peak was subsequently ascribed to As^{76}, while the Sb content indicated in the table is only the upper limit of the concentration of the impurity which can be determined in the given sample. The sharp rise in the curve in the initial section of the spectra is determined by the x-ray radiation of Tl^{204} and partially by the Compton contribution of the impurity elements. The spectra of samples Nos. 0 and 145 are shown in Fig. 5. The absence of Zn photo peaks is explained by the fact that the sharp rise in the curve, and the very low Zn content do not permit even an approximate evaluation of its content in these samples. The lowest curve in Fig. 5 is the spectrum of the background.

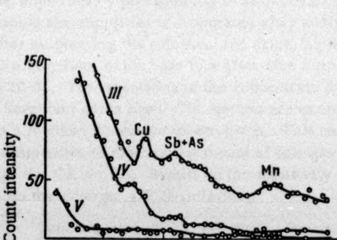

Fig. 5. Spectra of thallium samples. III) Spectrum of sample No. 0; IV) spectrum of sample No. 145; V) spectrum of the background.

Quantitative determination of the impurities was carried out by comparing the areas or the heights of the photo peaks of the test sample and of the standards, referred to the same measurement time. Correction for the geometry was not introduced, since the samples and the standards were measured under identical conditions.

The mass of the test impurities was calculated by means of the equation $m_{sample} = m_{standard} \cdot S_{sample}/_{standard} \cdot K$, where m_{sample} is the mass of the test element; $m_{standard}$ is the mass of the standard; $m_{sample}/S_{standard}$ is the ratio of peak areas or peak heights of the photo currents; K is a correction for the chemical yield of the standard.

After calculating the absolute mass of the impurity, its content in the sample was calculated (in %).

Results of the analysis of thallium samples for the impurities listed above are given in the table.

An examination of the table shows that the Sb content of all four samples, and the Mn content of two of them, is less than the sensitivity of the determination. Some ideas relating to an evaluation of the sensitivity of the determination of Sb have been described above; while an evaluation of the sensitivity of Mn determination in samples Nos. 2 and 145 was carried out by the method of additions.

SUMMARY

A method has been developed for the determination of Mn, Cu, Zn, As, and Sb present as impurities in high purity thallium.

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CHEMICOSPECTROGRAPHIC DETERMINATION OF IMPURITIES IN THORIUM AND ITS COMPOUNDS

A. G. Karabash, Sh. I. Peizulaev, V. P. Usacheva,
G. G. Morozova, V. M. Meshkova, and V. L. Lobanova

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Some information on the determination of impurities in pure metallic thorium and its compounds has been published [1-6]. Chemical analytical methods are very complicated [2, 3]. Spectrographic analysis of thorium is also difficult because of the high degree of complexity of the emission spectrum of the base. Accordingly, in order to determine impurities with a high degree of sensitivity, either carrier methods (e. g., Ga_2O_3), or spectrographs with a high resolving capacity [1, 7, 8], or an evaporation method are used [9].

During chemicospectrographic determination of impurities in thorium, the impurities are concentrated chemically and then determined spectrographically. The characteristics of the method used are the same as those described previously [10, 11]. Concentration of the impurities is carried out by almost complete removal of the base (thorium) by two techniques: by precipitation of thorium as its oxalate or in the form of its peroxide. A concentrate of the impurities is prepared from the mother liquor and beryllium oxide added as a base. This permits determination of a large number of elements with a high sensitivity on a spectrograph with average dispersion, since the spectrum of the concentrate of the impurities is freed from the thorium lines (see Figs. 1 and 2).

A Chemicospectrographic Method Involving Removal of Thorium as Its Oxalate. Thorium is removed from the impurities by precipitating it as the oxalate from a weakly nitric acid medium. The aqueous solution containing the impurities is evaporated after addition of beryllium nitrate, it is then treated with ammonia, and, after evaporating the solution, and calcining the residue, a powdered concentrate of the impurities is obtained on a beryllium oxide base in a glass-like form. The enrichment coefficient of the impurities in the concentrate is 20-30. The impurities in the concentrate are determined spectrographically, using standards also prepared on a beryllium oxide base. The spectra are excited in a dc arc between carbon electrodes, and are photographed on a medium dispersion spectrograph. This method permits determination of the following 18 elements present as impurities in thorium, by means of one spectrogram: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Sb. Results on the sensitivity of the method are given in Table 1. The accuracy of the method is on the average ± 20% (relative).

Concentration of the Impurities. Precipitation of thorium by oxalic acid is a fairly selective method, and was accordingly used for concentrating the impurities during their determination in thorium. According to published results [2], it is possible to separate thorium from the alkali and alkaline earth metals, Fe, Al, Cr, Co, Ni, Zn, Be, Ga, Ti, Zr, and U. The following conditions were chosen for precipitating the oxalate, these conditions ensuring fairly complete separation of thorium, and minimum coprecipitation of impurities: a) precipitation is carried out in a weakly acid medium (1 N HNO_3) from hot solution by gradual addition of precipitant while the solution is stirred; b) the precipitate plus mother liquor are kept on a water bath for recrystallization and self-purification; c) during precipitation, oxalic acid amounting to 80% of the stoichiometric amount is first added, while after a certain time the remainder of the precipitant is added in twofold excess. It was found that when this method of precipitation was used—by addition of the oxalic acid in two lots—the thorium oxalate precipitate

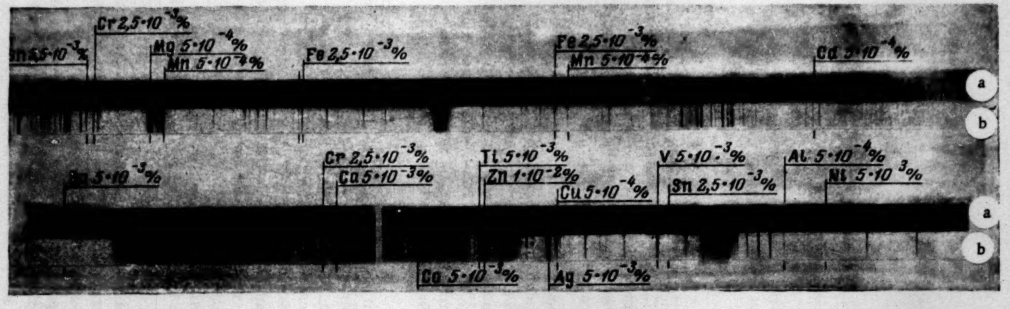
Sn 5·10-3%
Cr 2,5·10-3%
Mg 5·10-4%
Mn 5·10-4%
Fe 2,5·10-3%
Fe 2,5·10-3%
Mn 5·10-4%
Cd 5·10-4%
a
b
Sn 5·10-3%
Cr 2,5·10-3%
Ca 5·10-3%
Ti 5·10-3%
Zn 1·10-2%
Cu 5·10-4%
V 5·10-3%
Sn 2,5·10-3%
Al 5·10-4%
Ni 5·10-3%
a
b
Co 5·10-3%
Ag 5·10-3%

Fig. 1. Spectrograms: (a) sample of thorium (as ThO_2); (b) concentrate of the impurities obtained from the same sample on a BeO base. The impurities were added artificially; concentration was carried out by the oxalate method, the enrichment coefficient being K = 9.

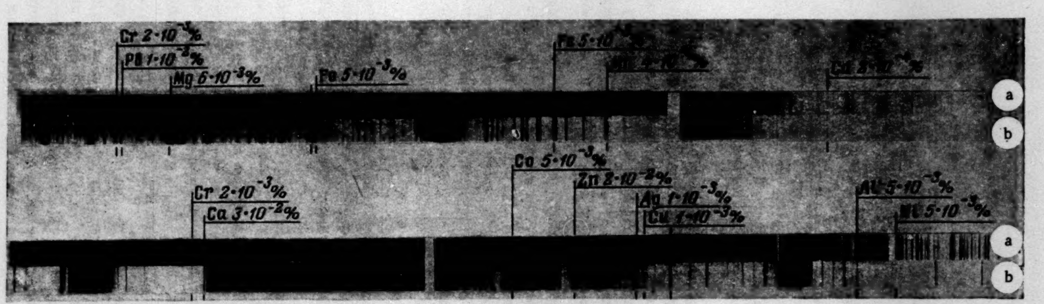
Cr 2·10-3%
Pb 1·10-2%
Mg 6·10-3%
Fe 5·10-3%
Fe 5·10-3%
a
b
Co 5·10-3%
Zn 8·10-2%
Cr 2·10-3%
Ca 3·10-2%
Ag 1·10-3%
Cu 1·10-3%
Al 5·10-3%
Ni 5·10-3%
a
b

Fig. 2. Spectrograms: (a) thorium sample (as ThO_2); (b) concentrate of the impurities from the same sample on a BeO base. The impurities were added artificially; concentration was carried out by the peroxide method, the enrichment coefficient being K = 2.5.

TABLE 1

Sensitivity of the Determination of Impurities in Thorium (K is the enrichment coefficient)

Element and analytical line	Precipitation method	
	oxalate with K = 20	peroxide with K = 5
Mg 2802,7	$2 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
Ca 4226,7	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ba 4934,1	$2 \cdot 10^{-4}$	$6 \cdot 10^{-4}$
Al 3082,2	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ti 3349,0	$1 \cdot 10^{-4}$	
V 3184,0	$5 \cdot 10^{-5}$	
Cr 2835,6	$5 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Mo 2816,2	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Mn 2576,1	$1 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
Fe 2599,4	$5 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Co 3412,6	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ni 3050,8	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Cu 3247,5	$1 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
Ag 3280,7	$2 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
Zn 3345,0	$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
Cd 2288,0	$5 \cdot 10^{-6}$	$2 \cdot 10^{-5}$
Sn 2840,0	$1 \cdot 10^{-4}$	
Sb 2598,1	$2 \cdot 10^{-4}$	
Pb 2833,1		$4 \cdot 10^{-4}$

obtained was very compact, almost half the volume of the precipitate obtained when all the oxalic acid is added at once. The amount of thorium left in the solutions when the precipitation conditions described above were used, as determined from data on the solubility of thorium oxalate [12] and according to experiments which we carried out, was very insignificant—not more than 1 mg in 100 ml of solution (usually 0.5-0.6 mg Th)—and did not interfere with subsequent spectrographic determination of the impurities in the concentrate. Published results [1] on the quantitative removal of traces of elements during precipitation of thorium oxalate were checked experimentally.

Various amounts of standard solutions of the impurity elements (from 1×10^{-4} to 1×10^{-1}% of each elements, calculated as the metal) were added to preparations of thorium nitrate* which had been specially purified and checked for the absence of impurities. These mixtures were taken through all the analytical stages involving removal of thorium as the oxalate. The distribution of the impurity elements between the solution and precipitate was established by analyzing each phase. For this purpose, the mother liquor was separated from the precipitate after the first precipitation, while the precipitate was calcined at 300°, dissolved in nitric acid, and then reprecipitated with oxalic acid. The mother liquor left from the first precipitation (the main impurity concentrate) and the solution left after the reprecipitation of the oxalate, were each analyzed spectrographically by the method described below. The balance for the distribution of the elements between the phases was then compiled. On the basis of these experiments, and also on the basis of experiments carried out for checking the analytical accuracy on synthetic mixtures (the object of the work) described below, it was established that the following elements, present as impurities, are almost completely extracted in the main impurity concentrated: Mg, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, Sb.

Traces of Ag were found to be concentrated in the nitric acid mother liquor. Under the conditions used, in the presence of traces of Cl^-, traces of Ag are completely concentrated for contents of less than 1×10^{-3} % Ag. Traces of Ca and Ba are concentrated completely when their contents are less than 1×10^{-2} %.

Completeness of extraction of traces of elements in the concentrate is 85-100% (Table 2). Quantitative extraction of a number of other elements (Fe, Co, Cr) was also checked chemically.

The efficiency of the removal of thorium and the concentration of the impurities is illustrated in Fig. 1, where a comparison is made of the spectrogram of a synthetically prepared sample of thorium dioxide, and that of a concentrate of the impurities obtained from the same sample.

Experimental Procedure. Preparation of the Chemical Concentrate. A three gram sample of metallic thorium is dissolved in aqua regia in a 300 ml quartz conical flask. Marks corresponding to volumes of 100 and 150 ml should be made on the flask. Dissolution is carried out carefully at first and then with vigorous heating. The black or yellow precipitate formed [13] should dissolved completely. The solution is evaporated almost to dryness, nitric acid being added to convert all the salts into the nitrates, 8 ml of concentrated nitric acid is then added and the volume of the solution diluted to 100 ml with water, i. e., until the HNO_3 concentration is about 1 N HNO_3. The solution is heated, and to the hot liquid is added slowly, with stirring, a hot 10% solution of oxalic acid which is measured out accurately at the rate of 2.64 g $H_2C_2O_4 \cdot 2H_2O$ per 3 g of thorium metal.

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* Purification was carried out by reprecipitating thorium oxalate until there were no impurities in the concentrate prepared from the mother liquor on a beryllium oxide base. The concentrate was analyzed spectrographically.

TABLE 2

Enrichment of Traces of Impurities in the Concentrate during Precipitation of Thorium

Elements (impurities)	Completeness of extraction during separation by precipitation (mean value), %	
	oxalate	peroxide
Mg	98	92
Ca	85	94
Ba	90	96
Al	99	90
Ti	99	—
V	95	—
Cr	98	98
Mo	85	97
Mn	95	94
Fe	100	96
Co	99	98
Ni	99	98
Cu	95	95
Ag	90	92
Zn	100	92
Cd	95	94
Sn	100	—
Sb	95	—
Pb	—	96

The solution plus the precipitate is kept for four hours on a water bath, and the second portion of the oxalic acid, amounting to 3.96 g per 3 g of Th, added in the same way. Water is added to bring the volume up to 150 ml, and the solution plus precipitate kept for one hour on the water bath, and for three hours at room temperature. An aliquot of the mother liquor (120 ml) is then carefully decanted, without disturbing the precipitate, into a beaker on which the volume has been marked out. The liquor which has been poured off is evaporated in a tared quartz basin, to which a solution of spectrographically pure beryllium nitrate containing 100 mg Be has been added. Three ml of concentrated HNO_3 is added, and the liquor evaporated to dryness, and calcined at 200-300° to remove excess oxalic acid. The residue is dissolved in 3 ml HNO_3 and is evaporated to a sirupy state. Beryllium hydroxide is precipitated by adding 25% ammonia with stirring, the precipitate is dried and calcined at 250-300° until all the ammonium nitrate has been removed, and then calcined at 500° for 30 min. The powdered concentrate obtained is weighed in order to determine the enrichment coefficient, it is then ground and analyzed spectrographically. Chemical concentrates of the impurities are made in the same way during the analysis of thorium compounds which are converted into the nitrate. The control test is taken through all the stages of the analysis using all the reagents.

Quartz vessels are used. The reagents—hydrochloric and nitric acids, ammonia, and water—are distilled in quartz vessels. Oxalic acid is purified by recrystallization. The beryllium nitrate solution which has a concentration of 40-45 mg Be/ml is prepared from beryllium acetate which has been purified by extraction with chloroform [14].

Note. Pb and Bi present as impurities are not completely concentrated during separation of thorium oxalate; they can be determined spectrographically after removal by extraction with sodium diethyldithiocarbamate and with dithizone in a separate aliquot of sample.

Spectrographic Determination of Impurities. Determination of impurities on a beryllium oxide base has been outlined in detail in another paper [14]. The spectra are photographed on a ISP-22 spectrograph, the slit width being 10 μ; a two stage attenuator with a relative percentage transmission of approximately 10 : 1 is fitted in front of the slit. The spectra are excited in a dc arc at a current strength of 10 amp. The exposure time is 2 min. The lower electrode (anode) has an opening with a diameter of 4 mm and a depth of 6 mm, while the upper electrode is a rod sharpened to a cone. The weight of the powdered concentrate or standards, on a BeO base, fed into one of the electrodes, is 50 mg. The powder in the opening of the electrode is moistened with two drops of a 20% alcoholic solution of Bakelite and is dried on a hot plate. Calibration curves are constructed within the coordinates (log I, log C), the background being taken into account, where I is the line intensity, and C is the concentration. The results obtained from the calibration curve are divided by the enrichment coefficient of the impurities in the concentrate in order to obtain their percentage contents in the original sample.

Chemicospectrographic Method with Separation of Thorium as its Peroxide. The given method differs from the preceding method by the technique used for concentrating the impurities. Thorium is removed from impurities by precipitating it with hydrogen peroxide from a weak nitric acid solution, and the precipitate centrifuged. After reprecipitation, the combined solutions are evaporated after addition of beryllium nitrate, the mixture is treated with ammonia and then dried; after calcination, a powdered concentrate of the impurities is obtained on a beryllium oxide base in a glass like form. The enrichment coefficient of the impurities in the concentrate is 2.5-5. The spectrographic analysis of the concentrate is carried out in the same way as that described in the previous section. By this method the content of the following 15 elements, present as impurities, is determined: Mg, Ca, Ba, Al, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb. The sensitivity of the method is given in Table 1. The accuracy of the method is characterized by an average relative error of ±20%.

Concentration of the Impurities. For separating thorium quantitatively and concentrating the impurities, the very selective reaction of precipitating thorium with hydrogen peroxide is used [1, 2, 15, 16]. According to

TABLE 3

Results of the Analysis of Synthetic Mixtures (Thorium removed as the peroxide)

Elements	Impurity content in percent, with respect to Th					
	Mixture No. 8		Mixture No. 9		Mixture No. 10	
	added	found	added	found	added	found
Mg	$7,5\cdot10^{-4}$	$6,0\cdot10^{-4}$	$7,5\cdot10^{-4}$	$6,0\cdot10^{-4}$	$2,0\cdot10^{-4}$	$1,7\cdot10^{-4}$
Ca	$1,0\cdot10^{-3}$	$1,1\cdot10^{-3}$	$1,0\cdot10^{-3}$	$9,0\cdot10^{-4}$	$5,0\cdot10^{-4}$	$4,0\cdot10^{-4}$
Ba	$2,0\cdot10^{-3}$	$3,2\cdot10^{-3}$	$2,0\cdot10^{-3}$	$3,0\cdot10^{-3}$	$1,0\cdot10^{-3}$	$1,2\cdot10^{-3}$
Al	$7,0\cdot10^{-4}$	$7,5\cdot10^{-4}$	$7,0\cdot10^{-4}$	$7,5\cdot10^{-4}$	$3,5\cdot10^{-4}$	$4,5\cdot10^{-4}$
Ti	$2,0\cdot10^{-3}$	$2,4\cdot10^{-3}$	$2,0\cdot10^{-3}$	$2,6\cdot10^{-3}$	$1,0\cdot10^{-3}$	$1,0\cdot10^{-3}$
V	$6,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$6,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$3,0\cdot10^{-4}$	$2,5\cdot10^{-4}$
Cr	$4,7\cdot10^{-4}$	$3,7\cdot10^{-4}$	$4,7\cdot10^{-4}$	$4,1\cdot10^{-4}$	$2,3\cdot10^{-4}$	$1,9\cdot10^{-4}$
Mo	$4,0\cdot10^{-4}$	$4,0\cdot10^{-4}$	$4,0\cdot10^{-4}$	$4,5\cdot10^{-4}$	$2,0\cdot10^{-4}$	$2,1\cdot10^{-4}$
Mn	$6,5\cdot10^{-5}$	$5,0\cdot10^{-5}$	$6,5\cdot10^{-5}$	$5,5\cdot10^{-5}$	$3,2\cdot10^{-5}$	$3,0\cdot10^{-5}$
Fe	$4,0\cdot10^{-4}$	$6,6\cdot10^{-4}$	$4,0\cdot10^{-4}$	$7,6\cdot10^{-4}$	$2,0\cdot10^{-4}$	$1,8\cdot10^{-4}$
Co	$1,2\cdot10^{-3}$	$1,7\cdot10^{-3}$	$1,2\cdot10^{-3}$	$1,6\cdot10^{-3}$	$6,0\cdot10^{-4}$	$6,0\cdot10^{-4}$
Ni	$4,0\cdot10^{-4}$	$6,0\cdot10^{-4}$	$4,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$2,0\cdot10^{-4}$	$2,7\cdot10^{-4}$
Cu	$4\cdot10^{-5}$	$5\cdot10^{-5}$	$4\cdot10^{-5}$	$5\cdot10^{-5}$	$2\cdot10^{-5}$	$2\cdot10^{-5}$
Ag	$6\cdot10^{-5}$	$8\cdot10^{-5}$	$6\cdot10^{-5}$	$1,0\cdot10^{-4}$	$3\cdot10^{-5}$	$3\cdot10^{-5}$
Zn	$6,0\cdot10^{-3}$	$8,5\cdot10^{-3}$	$6,0\cdot10^{-3}$	$9,5\cdot10^{-3}$	$3,0\cdot10^{-3}$	$4,0\cdot10^{-3}$
Cd	$2,0\cdot10^{-5}$	$2,5\cdot10^{-5}$	$2,0\cdot10^{-5}$	$2,5\cdot10^{-5}$	$1,0\cdot10^{-5}$	$6\cdot10^{-6}$
Sn	$4,0\cdot10^{-4}$	$4,7\cdot10^{-4}$	$4,0\cdot10^{-4}$	$4,5\cdot10^{-4}$	$2,0\cdot10^{-4}$	$2,0\cdot10^{-4}$
Sb	$6,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$6,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$3,0\cdot10^{-4}$	$2,5\cdot10^{-4}$

published data, precipitation of thorium as its peroxide in neutral or weakly acid solution permits its separation from many foreign elements, and this method is recommended for determining thorium in ores with a complex composition [2, 3]. The composition and the nature of the thorium peroxide precipitate are strongly dependent on the precipitation conditions. In weakly acid media, a white, opaque, bulky precipitate is formed which has a variable composition, and which has only a very weakly expressed crystalline structure containing anions (NO_3^-, Cl^-, etc), and is strongly hydrated [1, 2]. In order to precipitate thorium completely and obtain a peroxide precipitate in a dense form, in which the minimum amount of impurities is entrained, the conditions usually recommended were chosen. Precipitation was carried out in a hot solution containing 5% NH_4NO_3, the original acidity of the solution being 0.1 N with respect to HNO_3. Acid concentrations greater than 0.3 N HNO_3 lead to some increase in the solubility of the precipitate. It should be borne in mind that during formation of thorium peroxide, an equivalent amount of acid is formed. After being allowed to stand, the thorium peroxide precipitate is removed by centrifugation from the mother liquor which contains the impurities. The volume occupied by the precipitate amounts to less than 10% of the total volume of solution.

For complete separation of the impurities, reprecipitation of the peroxide is specified. Under the experimental conditions, thanks to almost complete separation of thorium, only traces of thorium remain in the concentrate of the impurities, these traces being considerably lower than the permissible limits of spectrographic analysis (equal to about 1% Th in the weight of the concentrate).

A check was made on the distribution of the impurity elements between the phases, and on their extraction into the concentrate under the conditions of the method developed. Standard solutions of 15-22 elements, in amounts ranging from 10^{-2} - 10^{-3}% of each element with respect to thorium, were added to aliquots of specially purified thorium nitrate. The thorium peroxide was precipitated and then reprecipitated, and the impurity concentrate prepared on a beryllium oxide base by the technique described below. In order to determine the amount of the impurities entrained by the centrifuged precipitate of thorium peroxide, the latter was dissolved in a nitric acid solution, and the peroxide again precipitated, as a result of which a second concentrate of the impurities was obtained. The first concentrate (the principal) and the second (check) were analyzed spectrographically by the method developed. On the basis of the analytical results obtained, a comparison was made of all the elements added and found in each fraction. On the basis of several series of such experiments, it was established that the completeness of extraction of 15 impurity elements into the concentrate amounts to about 90-98%, as indicated in Table 2.

TABLE 4

Results of the Analysis of Synthetic Mixtures (Thorium removed as the peroxide)

Elements	Impurity content in percent, with respect to Th			
	Mixture. No. 13		Mixture No. 28	
	added	found	added	found
Mg	$1{,}0\cdot10^{-2}$	$9{,}3\cdot10^{-3}$	$4{,}0\cdot10^{-3}$	$3{,}6\cdot10^{-3}$
Ca	$3{,}0\cdot10^{-2}$	$3{,}7\cdot10^{-2}$	$1{,}2\cdot10^{-2}$	$1{,}5\cdot10^{-2}$
Ba	$5{,}0\cdot10^{-2}$	$4{,}2\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$2{,}0\cdot10^{-2}$
Al	$5{,}0\cdot10^{-2}$	$6{,}8\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}7\cdot10^{-2}$
Cr	$2{,}0\cdot10^{-2}$	$1{,}7\cdot10^{-2}$	$8{,}0\cdot10^{-3}$	$8{,}4\cdot10^{-3}$
Mo	$1{,}0\cdot10^{-2}$	$1{,}4\cdot10^{-2}$	$4{,}0\cdot10^{-3}$	$4{,}2\cdot10^{-3}$
Mn	$4{,}0\cdot10^{-3}$	$3{,}5\cdot10^{-3}$	$1{,}6\cdot10^{-3}$	$1{,}3\cdot10^{-3}$
Fe	$2{,}0\cdot10^{-2}$	$2{,}1\cdot10^{-2}$	$1{,}2\cdot10^{-3}$	$1{,}2\cdot10^{-3}$
Co	$5{,}0\cdot10^{-2}$	$3{,}4\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}9\cdot10^{-2}$
Ni	$5{,}0\cdot10^{-2}$	$3{,}8\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}9\cdot10^{-2}$
Cu	$3{,}9\cdot10^{-3}$	$4{,}0\cdot10^{-3}$	$2{,}7\cdot10^{-3}$	$2{,}3\cdot10^{-3}$
Ag	$4{,}7\cdot10^{-3}$	$4{,}7\cdot10^{-3}$	$3{,}2\cdot10^{-3}$	$2{,}1\cdot10^{-3}$
Zn	$1{,}0\cdot10^{-1}$	$7{,}8\cdot10^{-2}$	$8{,}0\cdot10^{-2}$	$5{,}0\cdot10^{-2}$
Cd	$1{,}0\cdot10^{-3}$	$5{,}5\cdot10^{-4}$	—	—
Pb	$3{,}0\cdot10^{-2}$	$3{,}1\cdot10^{-2}$	$1{,}2\cdot10^{-2}$	$1{,}0\cdot10^{-2}$

Ti, V, Sn, and Sb are coprecipitated with thorium peroxide, and cannot be determined. The fact that almost complete concentration of traces of the elements is achieved, was also confirmed by analysis of synthetic mixtures (problem) during a check on the accuracy of the method (see below). The efficiency with which the base is removed, and the impurities concentrated, is illustrated by a comparison of the spectrograms of samples and concentrates in Fig. 2.

Experimental Procedure. Preparation of the Chemical Concentrate. An aliquot of thorium metal weighing 0.250 g is dissolved in aqua regia in a quartz beaker. Heating is continued until the black or yellow precipitate has dissolved. The solution is evaporated three times almost to dryness, nitric acid being added to convert the salts to nitrates. The dry salts are dissolved on heating in 3 ml of water to which 1 ml of 5 N HNO_3 has been added. Water is added to bring the volume up to about 40 ml, and 2 g of crystalline, spectrographically pure ammonium nitrate added. The weakly nitric acid solution obtained, which has an acidity of about 0.1 N HNO_3, is heated to 60-80°, and 10 ml of a 15% H_2O_2 solution added slowly, with stirring, until thorium peroxide has been completely precipitated. After standing for one hour, the solution is removed from the precipitate by centrifuging in a quartz test tube. The beaker walls are rinsed three times with 3 ml portions of 1% NH_4NO_3 solution. The thorium peroxide precipitate is dissolved in 7 N HNO_3, the solution is evaporated, and the peroxide reprecipitated under the conditions outlined above. The solutions separated from the precipitate are poured into a tared quartz basin, a solution of spectrographically pure beryllium nitrate containing 100 mg Be is added, and the liquid evaporated to a sirupy state. The hydroxides are precipitated with excess of 25% ammonia, they are dried and then calcined at 250-300° to remove the ammonium nitrate; they are finally calcined at 500° for 30 min. The concentrate of the impurities on a BeO base is weighed in order to determine the enrichment coefficient, and is then analyzed spectrographically. A blank test is carried out in parallel, the same reagents and identical conditions being used. All operations are carried out in quartz vessels. Water, acids, and ammonia are redistilled in quartz apparatus, as well as the hydrogen peroxide (under vacuum). Ammonium nitrate is prepared by neutralizing redistilled nitric acid with ammonia.

The spectrographic analysis is carried out by the technique outlined above.

The accuracy and reproducibility of the two variants described above for the chemicospectrographic method were checked by analyzing synthetic mixtures. The mixtures were prepared by addition to thorium nitrate preparations which had been purified beforehand by several reprecipitations (as the oxalate or peroxide, respectively), of standard solutions of 15-20 elements in amounts ranging from 10^{-3} to 10^{-5}% (with respect to thorium). The synthetic mixtures, as well as the thorium nitrate preparations used, were subjected to complete analysis by the appropriate method. Examples of the analyses of several mixtures are given in Tables 3 and 4.

SUMMARY

Two variants of a chemicospectrographic method for the determination of traces of impurities in thorium and its compounds have been developed. In the first of these variants, the impurities are concentrated by separating thorium as its oxalate from a weak nitric acid medium; the enrichment coefficient of the impurities is 20-30. In the second variant, the impurities are concentrated by separating thorium from a weak nitric acid medium in the form of its peroxide; the enrichment coefficient is 2.5-5. In both variants, the powdered concentrate obtained on a beryllium oxide base, after evaporating the solution of the impurities, is spectrographically analyzed; the spectra are excited in a dc arc and photographed on a quartz spectrograph having average dispersion.

Eighteen elements: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Sb are determined simultaneously on one spectrogram when the first variant is used; while when the second variant is employed 15 elements can be determined: Mg, Ca, Ba, Al, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb.

Owing to removal of the thorium, and concentration of the impurities, the sensitivity with which they can be determined is correspondingly increased (to 10^{-4} - 10^{-5} %).

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A RAPID MICROMETHOD FOR THE DETERMINATION OF SULFUR IN MONOMERIC AND POLYMERIC ORGANIC COMPOUNDS IN THE PRESENCE OF HALOGEN, NITROGEN, AND THE ALKALI METALS

A. I. Lebedeva and I. V. Novozhilova

Institute of High Molecular Weight Compounds,
Academy of Sciences, USSR, Leningrad

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A considerable number of articles have been published on the development of methods for the quantitative determination of sulfur in organic and inorganic compounds [1-11]. When halogens, nitrogen, and the alkali metals are also present, sulfur is determined titrimetrically [2-4, 6, 9] or gravimetrically [5]. The most suitable method from our point of view proved to be Boetius' method [4], which consists in combustion of an aliquot of the test compound in a flask filled with oxygen, followed by titration of the sulfuric acid formed by barium nitrate using sodium alizarinsulfonate (alizarin red S) as indicator.

Precipitation of barium sulfate under various conditions has been studied in detail by Geyer [1] who used a number of inorganic compounds. Boetius et al adopted Geyer's method for the analysis of organic compounds containing other elements (halogens, nitrogen, and the alkali metals) in addition to sulfur. When, however, we checked this method, it was found that Boetius' method as described did not contain sufficient detail (in particular, the weight of sample taken was not indicated), and accordingly we did not obtain positive results.

In the work described here we studied the analytical stages separately, and we have given a detailed description of a technique for the quantitative determination of sulfur in monomers and polymers containing halogens, nitrogen, and the alkali metals.

We found out that readily reproducible results are obtained when the test mixture is completely free from hydrogen peroxide which is normally used for oxidizing the sulfur oxides formed to SO_3; complete removal of hydrogen peroxide was effected only by evaporating the contents of the flask in the presence of platinum black until the moist salts were obtained. Evaporation to the moist salt state has the added advantage that it is then possible to establish the desired ratio of the organic and aqueous phases (1 : 1) accurately [1].

By modifying individual details in the analytical procedure and the ratios of the reagents, we obtained completely satisfactory results for materials containing from 2 to 40% of sulfur (see Table 1).

Table 2 contains results for the determination of sulfur in polymeric compounds when the flask combustion method was used, and also results obtained by the hydrogenation method [12].

Experimental. Aliquots of the test material were burnt in 250 ml conical flasks filled with oxygen. The apparatus and technique of the oxygen flask combustion method have been described in detail in the paper by Sokolova et. al., [13].

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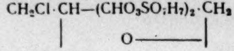
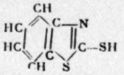
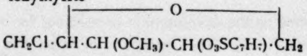
[*] 2-3 drops of formalin can be added instead of platinum black.

TABLE 1

Sample Weight 2-6 mg; 5 ml acetic acid (2 : 3); 1 ml of 0.5 N NaOH; 3 drops of a 0.1% aqueous solution of sodium alizarinsulfonate; ethanol : water = 1 : 1; total volume 20 ml

Test material	Sample wt., mg	0.02 N $Ba(NO_3)_2$ used, ml	S content, %	
			found	calc.
Ditozylmonochlorohydrin of xylylthane	6,210	2,68	13,84	13,91
 $CH_2Cl\cdot CH-(CHO_3SO{;}H_7)_2\cdot CH_2$	5,790	2,51	13,90	
Diphenylthiourea	3,920	1,72	14,07	14,04
$S=C(NHC_6H_5)_2$	4,720	2,03	14,13	
2-Mercaptobenzthiazole (Captax)	2,540	3,04	38,22	38,34
	2,020	2,41	38,26	
p-Thiocyanatochlorobenzene	2,920	1,71	18,78	18,88
$p-ClC_6H_4SCN$	3,750	2,18	18,64	
Sodium β-sulfopropiononitrile	4,510	2,85	20,26	20,36
	3,930	2,50	20,40	
2,5-Anhydro-1-chloro-3-methoxy-4-tozylxylite	5,290	2,25	13,64	13,91
 $CH_2Cl\cdot CH\cdot CH(OCH_3)\cdot CH(O_3SC_7H_7)\cdot CH_2$	5,330	2,26	13,91	
Sodium bromoethanesulfonate	5,050	2,35	14,93	15,19
$BrCH_2\cdot CH_2SO_3Na$	3,770	1,74	14,81	
Ditozylmonochlorohydrin mixture	4,870	2,08	13,70	13,91
Xylethane C	5,380	2,31	13,77	
p-Dibromobenzene	~3,500			

A mixture of 10 ml of twice distilled water, 1 ml of 0.5 N NaOH, and 2-3 drops of 30% hydrogen peroxide was used as the absorption solution.

After an aliquot of sample had been burnt, and the combustion products had been absorbed for 8-10 min, the flask stopper and the platinum grid were rinsed with 50 ml of twice distilled water. The contents of the flask were evaporated to the damp salt state in the presence of a small amount (about 200 mg in two parallel samples) of platinum black [14] to remove excess peroxide. Five ml of water and 5 ml of dilute (2 : 3) acetic acid were added to the flask, and the mixture boiled for one minute (no longer) to remove CO_2. Ten ml of ethanol and three drops of a 0.1% aqueous solution of sodium alizarinsulfonate were added to the cooled solution, which thereby acquired a yellow color. When the solution had a rose or a distinctly rose tinge after addition of the alcohol, then a further small amount of acetic acid (0.5-1 ml) was added until the color changed to yellow. The contents of the flask were titrated with 0.03 N $Ba(NO_3)_2$ until the color changed to rose. Just before the end point, titration was carried out slowly, and the color of the solution being titrated was compared with the color of a sample whose determination had been carried out in parallel. Two drops of reagents were sufficient to change the color.

The amount of sample taken is altered in accordance with the percentage sulfur content of the test compound. For compounds containing 10-20%, 20-30%, and 30-40%, sample weights of 4-5, 3-3.5, and 2-2.5 mg are recommended.

When the sulfur content is very low the sample weight can be increased to 8-10 mg.

TABLE 2

Determination of Sulfur in Polymeric Compounds*

Sample No.	S content, %		Sample No.	S content, %	
	by combustion in a flask	by hydrogenation**		by combustion in a flask	by hydrogenation**
1	8,02 7,81	7,73	5	6,04 5,79	5,57
2	9,19 9,12	9,19	6	5,32 5,42	5,29
3	7,26 7,30	7,23	7	5,54 5,50	5,49
4	8,85 8,62	8,86			

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[*] The polymeric compounds contained sulfur, chlorine, and nitrogen in addition to carbon, hydrogen, and oxygen; sample No. 6 also contained sodium

[**] E. S. Pisarenko carried out the hydrogenation method of analysis.

The $Ba(NO_3)_2$ solution was standardized against chemically pure grade K_2SO_4 (heated to constant weight at 105°) by a method similar to that mentioned above (without any addition of peroxide and platinum black); 1 ml of 0.02 N $Ba(NO_3)_2$ = 0.32066 mg S.

SUMMARY

A technique for the rapid microdetermination of sulfur in organic monomeric and polymeric compounds is described. Sulfur (2-40%) can be determined (with an accuracy of ± 0.3%) in materials containing chlorine, bromine, nitrogen, and the alkali metals.

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A GENERAL METHOD FOR THE QUANTITATIVE DETERMINATION OF THE ANHYDRIDES AND CHLOROANHYDRIDES OF CARBOXYLIC ACIDS

L. M. Litvinenko, D. M. Aleksandrova,
and V. G. Napadailo

A. M. Gor'kii Khar'kov State University

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It was shown in 1956 [1] that the reaction of anhydrides and chloroanhydrides of carboxylic acids with aromatic amines is a very promising basis for the determination of these anhydrides, excess of amine being titrated potentiometrically by a diazometric method [2]. The suggested method has, however, only proved to be effective in the case of halogenoanhydrides. With the anhydrides, this method has proved to be suitable only for the most reactive ones (acetic and maleic anhydrides). Thus, in order to get complete reaction in the case of benzoic anhydride, it was necessary to heat it with an aromatic amine in a nitrobenzene solution at 150° for two hours, while such compounds as phthalic and succinic anhydrides could not be quantitatively converted into their amides even after several hours heating.

Recently we were able to show that carboxylic acids, on addition to an inert solvent, very strongly catalyze the reaction of an aromatic amine with anhydrides and chloroanhydrides [3-5]. Depending on the nature of the acid added and its concentration, it has been shown that the rate of acylation can be increased a few thousand times; it was also demonstrated that anhydrides which are normally inert in such reactions are particularly susceptible to this catalytic action. The discovery of this effect has made it possible to develop a more general and universal method for the determination of anhydrides and halogenoanhydrides of carboxylic acids, than the one we suggested earlier [1] (compare [6]).

EXPERIMENTAL

More than 20 aromatic and aliphatic anhydrides and chloroanhydrides were tested; equally good results were obtained. The most typical examples are given in the table.

Each of the test materials was subjected to a purification which ensured almost 100% pure products. By dissolving accurately weighed aliquots of these materials, 0.2 M solutions in an organic solvent were prepared; 0.2 ml lots of this solution were used for analysis.

Meta-chloroaniline was chosen as the amine, since it had the advantages over other amines, of giving better results during its titration, and of being readily acylated in mixtures of inert solvents and acetic acid. Samples of this amine which had been carefully purified for kinetic research [4], as well as samples obtained by a double distillation, proved to be equally suitable.

It was established that determinations can be carried out equally readily in benzene and nitrobenzene (both chemically pure grade solvents which had been dried and redistilled beforehand); nitrobenzene, however had the decisive advantage of being an outstanding solvent.

Test material	Sample wt., mg	Medium	Heating time, min	Mean value from several determinations
Acetic anhydride	4,08	NB + HAc	3	99,2±0,4
» »	4,08	B + HAc	5	99,1±0,3
Benzoic anhydride	9,07	NB + HAc	5	100,0±0,3
» »	9,07	B + HAc	10	100,3±0,1
Maleic anhydride	3,92	NB + HAc	3	100,2±0,4
Phthalic anhydride	5,91	NB + HAc	30	100,0±0,8
Succinic anhydride	3,99	NB + HAc	60	100,4±0,4
Acetyl chloride	3,14	NB + HAc	3	99,6±0,4
Benzoyl chloride	5,62	NB + HAc	3	99,6±0,5
»	5,62	B + HAc	5	99,5±0,6
p-Nitrobenzoyl chloride	7,42	NB + HAc	3	100,2±0,5

Note: B = benzene; HAc = acetic acid; NB = nitrobenzene

Initially we carefully purified and dehydrated the acetic acid as recommended in a previous article [7]; we subsequently established that chemically pure grade glacial acetic acid could be used without further purification. It should, however, be emphasized that some commercial glacial acetic acid contains traces of acetic anhydride as an impurity and this can lead to incorrect results. It is therefore essential to check, as indicated below, on the stability of solutions of m-chloroaniline in the acetic acid--inert solvent mixture.

Before carrying out any determinations,it is essential to carry out control tests to ensure that the solutions and the solvents used are free from materials which can react with sodium nitrite in an acid medium.

Solution of m-Chloroaniline in an Inert Solvent. In 100 ml of benzene or nitrobenzene, 0.35 g of the amine is dissolved; the solution is stored in a ground glass stoppered flask. The amine concentration remains unchanged for at least a month.

Determination of Sodium Nitrite Solution : m-Chloroaniline Ratio. Exactly 0.4 ml of a 0.2 M solution of m-chloroaniline in benzene or nitrobenzene was transferred to a 100 ml beaker; 10 ml of glacial acetic acid, 1 ml of 8% hydrochloric acid, and 0.5 g of solid potassium bromide were then added; the mixture was diluted to a volume suitable for titration (40-50 ml) and the amine titrated at room temperature with 0.01 M sodium nitrite solution from a 10 ml microburet having scale divisions of 0.02 ml, as in the method published earlier [2]. The emf was measured after the stirrer was switched off and the layers had separated. Care was taken to ensure that the platinum electrode was completely immersed in the aqueous layer. The mean value obtained from several such determinations was used for all subsequent determinations.

Testing for Absence of Acetic Anhydride in Acetic Acid. A mixture of 0.4 ml of a 0.2 M solution of m-chloroaniline in benzene or nitrobenzene and 0.4 ml of glacial acetic acid was kept at 70° for two hours; in the absence of anhydride,the amount of amine taken remained constant. It decreased significantly only on heating the mixture for four hours at 90-95°. When such a long period of heating is necessary in the course of a particular determination, control tests must be carried out.

Acylation. 0.4 ml of glacial acetic acid and 0.6 ml of 0.2 M m-chloroaniline in benzene or nitrobenzene were introduced into a test tube (100 ml long and 10 mm diameter): an aliquot (0.04 mM) of the test anhydride or chloroanhydride was then added. The mixture was thoroughly mixed, the test tube was connected to an air condenser and placed on a water bath at 65-70°. Depending on the anhydride taken, the heating time varied from three minutes to one hour. After being cooled, the contents of the test tube were rinsed with several portions (a total of 10-15 ml) of glacial acetic acid into a titration beaker, and the excess m-chloroaniline titrated as indicated above.

The anhydride content was calculated by means of the following formula:

$$P = \frac{M\alpha N\cdot 100\,(v_1 - v_2)}{A},$$

where M is the molecular weight of the anhydride or chloroanhydride, A is the sample weight (mg), N is the normality of the nitrite solution, $\underline{\alpha}$ is the correction factor for the normality. v_1 and v_2 the volumes of nitrite (ml) used for titrating the amount of m-nitroaniline taken for the acylation and for titrating excess of the amine.

Results for determination of anhydrides and chloroanhydrides are given in the table.

Statistical treatment of the results obtained [8] showed that the accuracy of the values obtained is not less than 1%.

For macrodeterminations, 0.05-0.1 M sodium nitrite and a 50 ml buret should be used, while the amount of test material, m-chloroaniline, solvent, and catalyst should be correspondingly increased.

SUMMARY

A general method has been developed for the quantitative determination of anhydrides and chloroanhydrides; it consists in treating the test material with excess m-chloroaniline in a mixture of an inert solvent and acetic acid (the catalyst), with subsequent back potentiometric titration of the residual amine with sodium nitrite. The method permits a rapid and fairly accurate (up to 1%) determination of both micro- and macroamounts of anhydrides and chloroanhydrides of carboxylic acids.

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DETERMINATION OF MONOHYDRIC PHENOLS BY PARTITION CHROMATOGRAPHY AND ULTRAVIOLET SPECTROPHOTOMETRY

I. M. Belova

All-Union Scientific-Research Institute of Metallurgical Thermal
Engineering, Sverdlovsk

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The present article is devoted to a study of the possibility of analyzing four component mixtures containing phenol and the isomeric cresols by partition chromatography (for separating the phenol mixtures) and ultraviolet spectrophotometry.

The method developed has been applied to the determination of phenols in drainage water from peat gas-generator stations and in the raw material used for plastics production. The mobile solvent used for chromatographic separation was isooctane, while the staionary phase was water.

Similar work already carried out was either with a different solvent, e. g., cyclohexane [1, 2] or with different phenols, when isooctane was used [3].

The discrepancies between published absorption coefficients [4, 5, 6] necessitated a fresh determination. Thus, in the case of p-cresol at $\lambda = 285.8$ mμ these discrepancies amount to about 12%, while for phenol at $\lambda = 271$ mμ, the discrepancies amount to 30-40%. For o- and p-cresols,they are not high.

Measurements were carried out on a SF-4 spectrophotometer in the spectral region 240-300 mμ, using quartz cuvettes with a layer thickness of 1 cm. Corrections for contamination of the cuvette were applied in all the determinations. Measurements were carried out at each wave length for the smallest slit width for which the sensitivity of the apparatus according to the potentiometer was still zero. The slit width was varied from 1.1 to 0.3 mm.

The absorption coefficients were determined for concentrations of 0.04-0.063 g/liter. During chromatographic separation, the concentration of the materials in the eluate lay mainly in the range 0.02-0.06 g/liter. At these concentrations, solutions of phenol and cresols in isooctane conform to Beer's law [5].

The optical purity of the isooctane (over the working range) was ensured by purifying the commercial product chromatographically.

The starting materials, which were contaminated by oxidation products, were purified by distilling them twice, and recrystallizing them once from optically pure petroleum ether. The exception was m-cresol, which was not recrystallized,and was accordingly not pure enough (b. p. 197°). Different melting points have been ascribed to phenol, o- and p-cresols, by different authors. The temperatures which we determined for our products agreed with the results given in [6-9]; they were 40.9° for phenol, and 30.9° and 34.9° for o- and p-cresols respectively.

In order to exclude errors as much as possible, both during weighing of the original materials, and during spectroscopic measurements (cleanliness of the curvette, setting the slit width and the wave length), 5-6 determinations of the absorption coefficient were carried out for each material. Freshly prepared solutions were used in each case, while the materials used for making up the solutions were recrystallized beforehand.

TABLE 1

Absorption Coefficients of Phenol, m-, and o-Cresols

Wave length	m-Cresol				o-Cresol				p-Cresol				Phenol		
	[4]	[5]	[6]	our results	[4]	[5]	[6]	our results	[4]	[5]	[6]	our results	[4]	[5]	our results
270	12,92	13,10	—	12,32	16,09	16,13	—	15,85	13,37	12,10	—	12,49	23,93	18,47	18,27
271	14,23	15,55	—	13,09	17,10	16,10	—	16,92	12,19	11,48	—	12,49	25,89	18,47	20,71
272	15,82	15,70	—	13,95	17,20	16,15	—	17,15	13,01	12,55	—	12,89	18,90	14,56	17,29
272,8	15,82	15,65	15,70	14,24	16,40	16,29	16,41	16,53	14,77	13,62	14,68	13,84	14,20	11,32	13,29
275	12,08	11,10	—	11,71	12,30	12,29	—	12,96	14,89	13,70	—	14,74	10,77	9,03	9,19
277,4	10,50	10,90	10,28	10,00	15,84	15,65	15,89	15,28	15,65	15,52	15,33	16,06	25,40	17,62	18,36
278	12,49	12,30	—	—	16,34	15,87	—	15,94	16,69	16,67	—	16,48	21,52	12,87	17,58
279	16,87	16,0	—	14,22	14,32	15,22	—	14,69	20,48	18,43	—	18,75	12,28	7,68	11,40
185,8	0,90	0,98	0,90	0,83	0,70	0,22	0,73	0,65	18,78	17,15	19,30	17,42	—	—	0,25

The mean arithmetic values of the absorption coefficients obtained are given in Table 1. With the exception of m-cresol, the values mainly lay between the published values [4-6].

When the mean values of the absorption coefficients were used in calculations during chromatographic separation of synthetic mixtures, a good balance among the materials was obtained.

Absorption curves of phenol and the cresols are shown in Fig. 1.

Table 2 contains the absorption maxima of the same materials. The biggest difference in the positions of the maxima according to our results and published data [4, 5] amounted to 0.8 mμ.

Silica gel prepared by Ramsey and Patterson's method [10] was the sorbent used. It should be pointed out, however, that silica gel prepared according to this method does not always prove suitable for use because of the formation of a large amount of fine particles, which are not removed on sieving through a 200 mesh sieve. The fine particles were removed by suspending the silica gel in water and siphoning off the upper layer. Ten minutes were allowed to elapse between making a suspension and siphoning off the upper layer [11]. The silica gel was dried at 100-105° for 24 hours. The silica gel fraction passing through a 100 mesh sieve but retained on a 200 mesh sieve was used for partitioning (American standard). After use the silica gel was regenerated by washing with distilled water.

The apparatus used (Fig. 2) for partition chromatography was similar in the main to that use by Sweeney and Bultman [3]. It consists of a column 18 mm in diameter and 300 mm long. It is possible to carry out partitioning under pressure in this apparatus. Nitrogen supplied from a cylinder supplied the pressure.

Before use, water and isooctane were mutually saturated with each other. Water was added to 19 g of silica gel in the maximum possible amount which still left the silica gel in the form of a dry powder (it does not cling to the walls and does not gelatinize in the isooctane). Taking into account the original moisture content of the silica gel, the amount of water added was slightly greater than 90 % by weight of the dry silica gel. One hundred ml of isooctane was then poured onto the silica gel; it was carefully freed from air bubbles and transferred to the column. When air bubbles appeared in the column they were removed by means of a glass rod. The sorbent was packed to give a column with a constant height by rotating the column in one direction. The silica gel column was finally packed by applying a pressure of 150 mm Hg. During packing, the sorbent took up 50-60 ml of isooctane. The height of the sorbent amounted to 180-195 mm.

TABLE 2

Absorption Maxima of Phenol and Cresols

	$\lambda_{max.}$, mμ			
	o-cresol	m-cresol	p-cresol	phenol
Our results	271,8; 278	272,6; 279,6	270,4; 273,4; 276,4; 279,2; 285,75	264,6; 270,8; 277,8
[4]	271,6; 277,8	272,4; 279,4	270; 273; 276; 279; 285,6	264,4; 270,8; 277,4
[5]	271; 278	272; 279	270; 272,8 276; 279; 285	265; 270; 277,4

It should be pointed out that in similar papers [1, 2], separation of phenolic mixtures was carried out using a column of sorbent with a different height although the diameter of the column was the same, i. e., 18 mm. When cyclohexane was used as the mobile solvent, separation of phenol and cresols occured on a silica gel column with a height of 500 mm (56 g). On a silica gel column with a height of 150 mm (19 g) only phenol is separated from the cresols. In our experiments,separation of the four component mixture of phenols occurred on a sorbent with a height of 500 mm; the weight of silica gel was 19 g,and this was sufficient to give the indicated height of packing. This, presumably, is determined by the partition coefficients of the test materials in the different solvent systems: cyclohexane—water and isooctane—water.

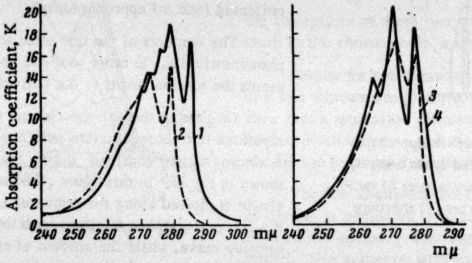

Fig. 1. Absorption curves in isooctane: 1) p-Cresol; 2) m-cresol; 3) o-cresol; 4) phenol.

A synthetic mixture of the following composition was used for partition chromatography: 0.451 g phenol/liter, 0.431 g o-cresol/liter, 0.414 g p-cresol/liter, and 0.359 g m-cresol/liter. The same materials as those used for determination of the absorption coefficients were used for preparing the synthetic mixtures. When the column had been prepared as indicated above, and the level of the solvent had reached the surface of the sorbent, but had not yet passed through it, 5 ml of a synthetic mixture was introduced into the column. The column walls were rinsed with a small amount of isooctane (2 ml) after the test sample had almost completely passed into the sorbent but the surface of the latter had not been exposed. This operation was repeated. The solvent flow and the pressure were then controlled so that the rate at which the eluate issued from the column was 2 ml/min. The eluate was collected in calibrated test tubes in 5 ml portions, from the moment at which the test sample was introduced into the column.

TABLE 3

o-Cresol			m-Cresol			p-Cresol			Phenol		
introd. into col.,%	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %
26,1	26,3 26,1	+0,2 0,0	21,3	21,6 22,1	−0,2 +0,3	25,0	23,3 23,6	−1,7 −1,4	27,2	28,9 28,3	+1,7 +0,9

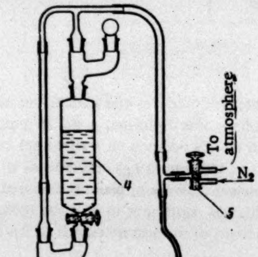

Fig. 2. Chromatographic apparatus. 1) Column; 2) sintered glass disc; 3) sorbent; 4) solvent container; 5) two-way tap; 6) manometer; 7) mercury trap.

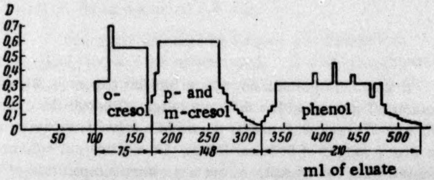

Fig. 3. Chromatogram of a synthetic mixtures of phenols.

When the flow rate is uneven and pulsating, clearly defined boundaries between the issuing materials are not obtained. When the elution rate is uniform, not less than 110 test tubes should be collected (550 ml approximately).

The contents of the test tubes were then examined spectrophotometrically. In order to speed up the spectrophotometric measurements the elution limits of the individual materials were determined.

On passing through the column the mixture of four phenols separates into three fractions with characteristic absorption curves. A chromatogram obtained during one of these experiments is shown in Fig. 3. In this figure, the maximum optical density of the eluate is plotted along the ordinate, i. e., the optical densities of the chromatographic fractions with the highest maxima on the absorption curve, while the amount of eluate (in ml) is plotted on the abscissa. In Fig. 3 the horizontal parts correspond to combined portions of the eluate, while the peaks correspond to the points at which the elution boundaries of the fractions were determined.

The concentration of the issuing component, and, accordingly, its optical density, increases from the point at which it appears in a given fraction; it then reaches a maximum and then falls right down to zero towards the end of elution (the family of curves in Figs. 4-6).

The order in which the fractions come through the column is o-cresol first (Fig. 4), this is followed by m- and p-cresol together (Fig. 5), and finally phenol (Fig. 6).

Before the appearance of o-cresol, pure solvent issues from the column, and this has an optical density of approximately 0.03 (at λ = 270 mμ). It was established experimentally that only 100 ml of pure solvent comes through, 65-110 ml with o-cresol comes next, followed by 150-175 ml with the mixture of p- and m-cresols, and approximately 200 ml with phenol.

The amount of o-cresol and phenol issuing separately was calculated by means of the formula:

$$g = \frac{D \cdot V}{K \cdot l} \tag{1}$$

where g is the amount of test material (g), D is the optical density, V is the volume of fraction being analyzed, K is the absorption coefficient (ml/cm), and l is the thickness of the absorbing layer (cm).

When such solvents as cyclohexane—water and isooctane—water are used, separation of m- and p-cresols to the individual compounds does not occur because of the small differences in the partition coefficients. Accordingly, the concentration of m- and p-cresols in the eluate was determined by solving the system of equations:

$$\begin{aligned} D_{\lambda_1} &= K^{(1)}_{\lambda_1} x_1 + K^{(2)}_{\lambda_1} x_2 \\ D_{\lambda_2} &= K^{(1)}_{\lambda_2} x_1 + K^{(2)}_{\lambda_2} x_2 \end{aligned} \tag{2}$$

In equations (2) x_1 and x_2 are the corresponding concentrations in g/ml.

It was established that results which showed the best agreement in the case of phenol and o-cresol are obtained at wave lengths corresponding to the widest absorption maxima of these compounds, namely: λ = 271.8 mμ and K_λ = 17151 for o-cresol, and λ = 270.8 mμ and K_λ = 20826 for phenol. In the case of m- and p-cresols, the best results were obtained at wave lengths corresponding to the following maximum for the combined absorption curve: λ_1 = 273 mμ and λ_2 = 285.75 mμ. For the wave lengths indicated the absorption coefficients are: K_{λ_1} = 14.170 and K_{λ_2} = 833 for m-cresol, and K_{λ_1} = 14.052 and K_{λ_2} 17.425 for p-cresol. The ratio of the absorptions of these two compounds is a maximum at the chosen wave lengths.

Results for two quantitative determinations of a test mixture are given in Table 3; these results show that a separation efficiency of not less than 0.5% is possible for o- and m-cresols, while for phenol and p-cresol this efficiency is 2%.

The low absorption coefficients obtained for m-cresol, as compared with published results, reflect on the accuracy with which p-cresol is determined. The accuracy with which p-cresol and phenol can be determined could be increased by determining the absorption coefficients of m-cresol and phenol more accurately.

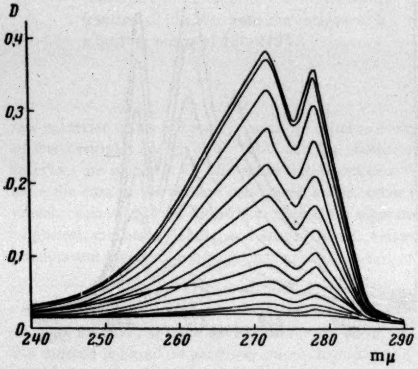

Fig. 4. Absorption curve of the first chromatographic fraction.

The method discussed has been used for establishing the presence of phenol and cresols in the residue from drainage water from peat gas-generator stations working on lowland peat. The residue is obtained by evaporating 85% of the acidified drainage water during purification, and could serve as a rich source of valuable chemicals, e. g., phenols. The lack of information on the chemical composition of the phenols in this drainage water from peat gas-generator stations, and lack of information on the residue, makes it difficult to choose the best way of using it. The residue was extracted with benzene and butyl acetate. Fatty acids were removed by treating the extracts with sodium carbonate solution. The phenols were isolated as phenates by treating the extracts with sodium hydroxide solution. The phenate solution was acidified, and the phenols extracted with ethyl ether; after evaporating off the ether and drying the residue over sodium sulfate, the residue was distilled under a vacuum of 5 mm Hg. Phenol and cresols were determined in the distillate, the temperature range of which reduced to 760 mm Hg was 180-230°. Thirty-two liters of the original water was required in order to obtain 10 g of phenols

TABLE 4

p-Cresol		Phenol	
in separate determinations, %	mean, %	in separate determinations, %	mean, %
3,0 2,8	2,9	33,8 34,3	34,0

TABLE 5

Phenol, %	p-Cresol, %	m-Cresol, %	Unknown, %
6,8	26,2	48,8	18,2
18,0	18,8	30,5	32,7
12,9	23,3	42,2	21,6

from the distillate, since the phenols content of the drainage water from the peat gas generating stations amounted to 5-7 g/liter of volatiles and 2-3 g/liter of nonvolatiles. When a test sample was analyzed by partition chromatography, three fractions were obtained as in the case of experiments with the synthetic mixture. The absorption curves of the first fraction, however, did not coincide with the curves for pure o-cresol. The absorption maxima of the subsequent fractions and of pure p-cresol proved to be the same and were found to be: 270.6-270.8; 273.0-273.4; 276.2-276.4; 279.4; 285.75 mμ.

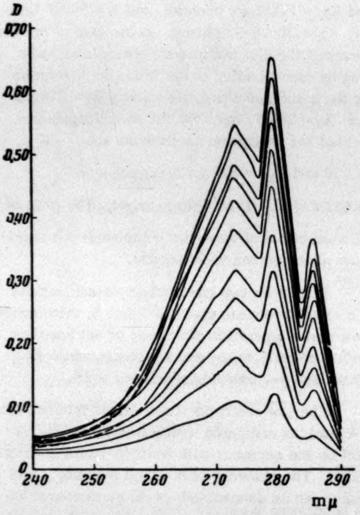

Fig. 5. Absorption curve of the second chromatographic fraction.

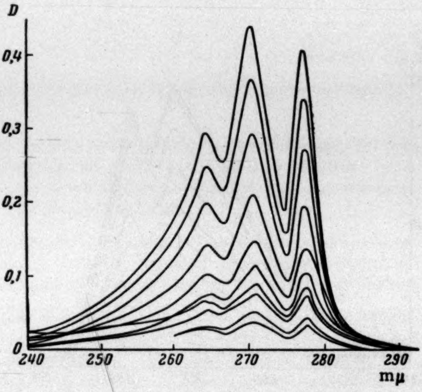

Fig. 6. Absorption curve of the third chromatographic fraction.

A comparison of the absorption curves of the given fraction with the curves for pure p-cresol shown in Fig. 7 shows that they are similar in shape. The test fraction therefore contains p-cresol.

The next fraction contains phenol, since the absorption curves of this fraction and of phenol are identical. Results of two parallel analyses of the test distillate obtained from the residue are given in Table 4. The deviation in the two parallel determinations amounts to 0.5% for phenol, and 0.2% for p-cresol. The phenol and p-cresol contents of the original water are therefore 0.0111 and 0.0095 g/liter · respectively.

During the analysis of so-called tricresols (raw material used for plastics production), we determined phenol, m- and p-cresols. The raw material was obtained from the "Plastmass" factory in Sverdlovsk where control of

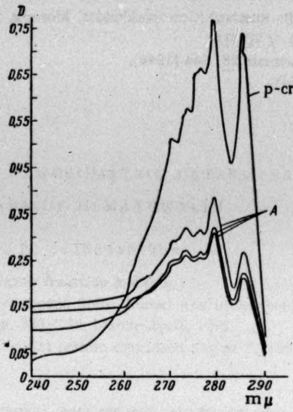

Fig. 7. Absorption curves of pure p-cresol and of the second chromatographic fraction of phenols from the residue with a boiling range of 180-230°.

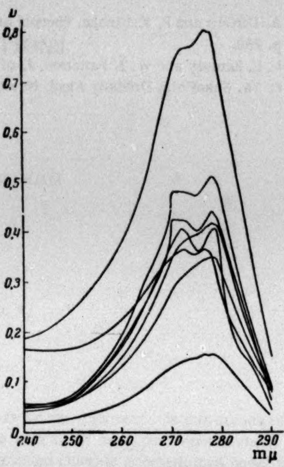

Fig. 8. Absorption curve of the chromatographic fraction issuing from the column before p- and m-cresols.

raw material is not carried out since no suitable analytical methods are available there. Results of the analysis of three samples are given in Table 5. The absorption curves of the fractions preceding the p- and m-cresols fractions are shown in Fig. 8; these curves indicate that the given fraction cannot be o-cresol. In this instance, as in the case of the residue mentioned above, other phenols presumably interfere with the determination of o-cresol. Pearson [2] has shown that during the separation of a thirteen component mixture of phenols consisting of phenol, cresols, xylenols, and ethyl phenols, o-cresol issues from the column with 2,4-xylenol, while the ethyl phenols and the remaining xylenols are eluted earlier.

SUMMARY

A method has been developed for the determination of phenol, o-, p-, and m-cresols in each others presence; the method is based on partition chromatography and ultraviolet spectrophotometry; isooctane is used as the mobile phase while water is used as the stationary phase. The experimental accuracy is not less than 2%.

Other phenol homologs interfere with determination of o-cresol.

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BRIEF COMMUNICATIONS

DIRECT FLUOROMETRIC DETERMINATION OF ALUMINUM BY MEANS OF HEMATOXYLIN

P. P. Solodovnikov

Kazan Aviation Institute

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At present there are still very few suitable and faultless methods for the volumetric determination of aluminum. According to Kolthoff [1], during titration of aluminum sulfate with alkali using phenolphthalein as indicator, the end point occurs before the equivalence point; when aluminum chloride is determined under the same conditions, the amount of alkali used corresponds to the theoretical value. Direct complexometric titration is unsuccessful even when alizarin S, stilbazo, chromazurol S, and other indicators are used. Since titration can only be carried out at pH 4.0 when these indicators are used, some of the aluminum is not complexed by sodium ethylenediaminetetracetate (EDTA-Na) [2]. Back titration of excess EDTA-Na with a standard $ZnSO_4$ solution with eriochrome black T, or with a $FeCl_3$ solution using salicylic acid [3], also possesses some drawbacks.

Our experiments have shown that the fluorometric method described by Tanaev [4] is worthy of attention. The method is based on formation of a sparingly soluble complex of the cryolite type $Na_3[AlF_6]$; trivalent iron and chromium ions form similar compounds.

During direct titration, a standard solution of the fluoride of an alkali metal is added to the test aluminum solution until some effect corresponding to an end point is observed. Excess fluoride could also be back titrated with a standard solution of an aluminum salt. Since an aqueous solution of an alkali metal fluoride has an alkaline reaction (pH 8.0), while that of an aluminum salt is acid (pH 3.5), when all the fluoride has been complexed, the excess of aluminum salt gives the solution an acid reaction which is detectable by the color change of methyl red or phenol red. Titration is carried out in the presence of NaCl in order to depress the solubility of the precipitate. Under these conditions, formation of $Na_3[AlF_6]$ proceeds even at pH 7.3-7.4 without simultaneous precipitation of $Al(OH)_3$. The method gives good results as long as certain conditions are observed; the main condition is the absence of free acids or alkalis in all the solutions; they will naturally distort the results, since titration is carried out with acid–base indicators.

The original materials used for preparing the working solutions must be purified most carefully when fluorometric titration is used. Aluminum preparations, even highly pure grade materials, may either contain free acid or basic salts; the latter liberate free alkali when they enter into reaction with fluoride ($Al[OH]^{2+} + 6F^- = [AlF_6]^{3-} + OH^-$). Alkali metal fluorides often contain Na_2SiF_6, Na_2SiO_3, Na_2CO_3, as impurities, these also form alkalis on hydrolysis. This means that during titration, the indicator acquires an intermediate color which interferes with exact establishment of the end point.

We set ourselves the problem of developing a method for the direct titration of Al^{3+} ions in which the end point is established, not by changes in the color of methyl red or phenol red, but by means of hematoxylin. The latter, although it belongs to the group of acid–base indicators for which the limits of the color change from yellow to violet are pH 5.0-6.0, does, in addition, possess the capacity of forming colored compounds with the ions of many metals. These compounds are regarded at present as inner complex compounds [5]. Such compounds, in most cases, are unstable in the presence of free acetic acid; under these conditions the color of the aluminum lac does not change.

TABLE 1

Aluminum taken, mg	Volume of KF solution (ml) and its normality	Aluminum found, mg	Difference, mg	Error, %
13,53	5,90 (0,499)	13,25	—0,28	2,0
12,04	5,25 (0,499)	11,79	—0,25	2,0
6,67	9,00 (0,1665)	6,74	+0,07	1,1
7,05	9,25 (0,1665)	6,98	—0,07	1,0
5,95	8,07 (0,1665)	6,04	+0,09	1,5
2,71	3,57 (0,1665)	2,67	—0,04	1,5
1,85	2,57 (0,1665)	1,88	+0,03	1,5
4,49	4,00 (0,2495)	4,49	0	
1,80	1,60 (0,2495)	1,80	0	
1,80	1,62 (0,2495)	1,82	+0,02	1,1

TABLE 2

Test material	Sample wt. mg	Amount of aluminum, mg	Volume of 0.128 N KF solution (ml)	Aluminum found, mg
Aluminum	10,06	9,97	17,32	9,97
Ditto	10,06	9,97	17,34	9,98
» »	10,06	9,97	17,35	9,99
Magnesium MLZ	50,7	0,98	1,70	0,99
Ditto	50,7	0,98	1,72	1,00
» »	50,7	0,98	1,73	1,01

Wildenstein [6] introduced hematoxylin $C_{16}H_{14}O_6 \cdot 3H_2O$ into analytical practice for the qualitative detection of the cations of certain metals (copper, lead, tin, antimony, etc.). Hematoxylin later found applications in photometric methods of analysis, although the literature published on these applications is small. Thus Hatfield [7] developed a method for controlling the content of aluminum compounds in water after purification of the latter. Tartakovskii [8] successfully used hematoxylin for the photometric determination of aluminum, tin, molybdenum, and chromium. Cherkesov and Busev [9] have recommended hematoxylin for spot test detection of antimony. Ch'ien Ts'ui Lin [10] introduced hematoxylin into complexometry for the indirect determination of aluminum.

The aluminum lac has a lilac or red-violet tinge which is preserved at pH 4.5-8.5; the composition of the compound varies with the analytical conditions, but this has no effect on the accuracy of the modified method which we have developed for the fluorometric titration of aluminum. According to Tartakovskii, the interaction of aluminum with hematoxylin proceeds as follows:

$$3C_{16}H_{14}O_6 + Al\,(OH)_3 = Al\,(C_{16}H_{13}O_6)_3 + 3H_2O.$$

We noticed that when an alkali metal fluoride is added to this compound in an acetic acid medium at pH 4.6-5.2, the compound is readily destroyed by fluoride ions, and the violet color of the lac disappears. The liberated hematoxylin colors the solution yellow, the latter being the characteristic color of the indicator itself in an acid medium. This process occurs at ordinary temperatures, but better at 50-60°.

Denoting the violet complex of aluminum with the dye by MeR the general scheme of the reaction can be written thus:

$$\begin{array}{cccc} \text{MeR} & +F^- \rightleftarrows & \text{MeF} & +R^- \\ \text{(Violet)} & & \text{(Colorless)} & \end{array}$$

TABLE 3

Al content of the solution, mg	Volume of 0.128 N KF, ml	Al found	
		mg	%
4,45	7,68	4,42	99,4
4,45	7,70	4,43	99,5
6,25	10,90	6,27	100,4
6,25	10,88	6,26	100,2
6,25	10,85	6,25	100,0

Babko [11] has shown that the ratio $[MeF] : [F^-] = K_{MeR} : K_{MeF}$ characterizes the extent to which the fluoride ions is complexed; it will be a maximum under conditions such that $K_{MeR} \gg K_{MeF}$, i. e., when the stability of the colored compound MeR is considerably less than that of the fluoride compound MeF of the same metal. Since the instability constant of the $[AlF_6]^{3-}$ is very small and is equal to 1.44×10^{-20}, the equilibrium of the reaction shown above can be regarded as being shifted almost completely to the right hand side.

This reaction was made the basis of a direct, and when necessary, a back fluorometric titration of aluminum in acetic acid medium using hematoxylin as indicator.

Standard solutions of potassium fluoride and aluminum sulfate whose ratio to each other is known are required. Hematoxylin is used as a 1% alcohol solution.

Technique. To a measured volume of a solution of an aluminum salt containing 2-10 mg of the latter, is added 1 ml of 30-40% acetic acid, and the volume made up to 25 ml with water. The solution is heated to 50-60° and sodium chloride added until the solution is saturated with it, 1-2 g of crystalline $NaC_2H_3O_2 \cdot 3H_2O$ is added and aluminum ions titrated with 0.2 N KF in the presence of hematoxylin until the violet color of the solution changes to a pure yellow which is the color of the acid form of the indicator.

To avoid precipitation of basic salts, sodium acetate should be added several times during titration in small portions, so that the acidity of the solution slowly drops to the requisite pH value as the end point is approached.

Toward the end of the titration the solution temperature should be kept at 50-60°.

If a back titration technique is adopted, a standard solution of aluminum sulfate (alum) is used, and titration is carried out from yellow to violet. The color change of the hematoxylin is sharp and reversible for forward and back titration.

It is only when the solution being titrated is allowed to stand for a long time that the color pales as a result of adsorption of the dye by the precipitated cryolite.

The color weakens and even completely disappears in solutions whose pH is below 4.5.

Experiments were carried out with solutions of chemically pure aluminum ammonium alums which had been standardized gravimetrically as Al_2O_3; in experiments Nos. 3, 4, 5, and 6 the solutions also contained magnesium, zinc, and manganese sulfates in the proportion of Al : Mg = 1 : 50 and Al : Zn (Mn) = 1 : 10.

Separate experiments showed that large amounts of iron, copper, tartrates, citrates, and oxalates in solution interfere with aluminum determination. In particular, as a result of formation of an iron lac, the color of the solution being titrated acquires a dirty tinge.

Results of some determinations are given in Table 1.

The method was also tried on aluminum metal grade A1, containing 99.5% Al and 0.5% Fe, Cu, and Zn and on magnesium metal (electron grade) containing 2% Al. Aliquots of these metals were dissolved in hydrochloric acid (1 : 1), and the aluminum determined on an aliquot of the solution (after adjusting the pH to 4.6-5.2).

Despite the lower solubility of magnesium and calcium fluorides in water (MgF_2 (18°)$-7.6 \cdot 10^{-4}$ g; CaF_2 (18°)$-1.6 \cdot 10^{-4}$ g in 100 g of water) [12] as compared with that of cryolite, when potassium fluoride is added to a solution containing Al^{3+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, and Mn^{2+}, the most stable complex ions $[AlF_6]^{3-}$ are formed first; consequently, aluminum is readily titrated in the presence of the other cations listed (Table 2).

Since the presence of a large amount of foreign salts during formation of colored lacs affects the shade of these lacs, the possibility of omitting sodium chloride was finally examined. Sodium chloride was replaced by ethanol, since Tananaev and Lel'chuk [13] have shown that ethanol supresses the solubility of cryolite in water appreciably. Thus, while the solubility of cryolite in water is 0.39 g/liter, this material is only soluble to the extent of 0.22 g/liter in 50% ethanol–water.

In our experiments the solutions being titrated contained 30% by volume of alcohol; the results obtained are given in Table 3.

SUMMARY

A method has been developed for the direct and back fluorometric titration of aluminum, using hematoxylin as indicator.

In contrast to the usual fluorometric titration of aluminum, using acid–base indicators in a neutral medium, hematoxylin permits determination to be carried out in an acetic acid medium at pH 4.8-5.0. Large amounts of copper, iron, tartrates, citrates, and oxalates should be absent. The method can be used for the determination of aluminum in the presence of magnesium (1 : 50), calcium, manganese, and zinc (1 : 10).

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GRAVIMETRIC DETERMINATION OF SMALL AMOUNTS OF LEAD BY MEANS OF A SOLUTION OF A DIVALENT CHROMIUM SALT

N. T. Vasina

Luganski State Medical Institute

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Numerous gravimetric, titrimetric, photometric, and other methods exist for the determination of lead [1-9]. Bearing in mind the various disadvantages of current methods of determining this element, we aimed at developing a new method for determining small amounts of lead in various materials by means of divalent chromium salt solution. Divalent chromium salts are very strong reducing agents [10-13]; they reduce arsenic, antimony, copper, tin, silver, and other ions to the elemental state.

Divalent chromium ions quantitatively reduce lead ions to the elemental state in acid media [14]. Our experiments have shown that there are no lead ions present in the filtrate left after filtering off the precipitate. A black precipitate of metallic lead separates out in the cold. The amount of lead is determined gravimetrically. Arsenic and zinc do not interfere with determination of lead by means of a divalent chromium salt. Antimony is partially coprecipitated with lead, but can be separated from the latter.

TABLE 1

Pb taken, mg	Pb found, mg	Pb taken, mg	Pb found, mg
4,0	3,8	2,0	1,8
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	1,0	1,0

The results given in Table 1 show that separation of lead by reduction with a divalent chromium salt solution gives satisfactory results.

Tables 2, 3, 4, and 5 contain results for the determination of lead in synthetic mixtures containing quinquevalent arsenic, zinc, and quinquevalent antimony. These results show that arsenic and zinc do not interfere with lead determination. Shat'ko [10] has shown that arsenic is precipitated from strongly acid solutions on heating (pH about 0.02). We therefore precipitated lead from solution at pH 3.7. Our experiments confirmed that under these conditions arsenic is not precipitated.

Divalent chromium ions quantitatively reduce quinquevalent antimony to the metallic state from neutral

TABLE 2

(20 mg As^V taken)

Pb taken, mg	Pb found, mg	Pb taken, mg	Pb found, mg
4,0	4,0	2,0	2,0
4,0	4,0	1,0	1,0
2,0	2,0	1,0	1,0

TABLE 3

(20 mg Zn taken)

Pb taken, mg	Pb found, mg
4,0	4,0
4,0	4,0
2,0	2,0
2,0	2,0
1,0	1,0
1,0	1,0

TABLE 4

(20 mg Sb^V taken)

Pb taken, mg	Pb found, mg
4,0	5,6
4,0	5,8
2,0	5,2
2,0	5,4
1,0	4,4
1,0	2,4

TABLE 5

Pb taken, mg	Pb found, mg
4,0	3,8
4,0	4,0
2,0	2,0
2,0	2,0
1,0	1,0
1,0	1,0

or weakly acid solutions [12]. Metallic antimony is oxidized by a standard solution of potassium dichromate in the presence of sulfuric acid (1 : 4). Under the experimental conditions used, antimony is partially precipitated with lead; incorrect results are therefore obtained for lead (Table 4).

To separate lead from antimony, we treated the precipitate on the filter with 0.2 N $K_2Cr_2O_7$ in a mixture with 20 ml of H_2SO_4 (1 : 4). Antimony thereupon dissolves, while the lead remaining on the filter is washed with 96% ethanol and dried at 105° to constant weight. The results obtained are given in Table 5.

Determination of small amounts of lead (about 1 mg/liter) is carried out as follows: the test solution is evaporated on a water bath to a volume of 10-25 ml, the solution is cooled to room temperature and 10-12 ml of 0.5 N $CrCl_2$ solution added, after 5-10 min the metallic lead is filtered off in a Schott No. 4 crucible, washed 2-3 times with 96% alcohol, and dried to constant weight at 105°.

The divalent chromium solution can be prepared by P. P. Shat'ko's electrolytic method [15] or by a modification of N. A. Popov's method [16].

SUMMARY

Divalent chromium ions quantitatively reduce divalent lead to the elemental state at pH 3.7 at room temperature. The precipitated lead is weighed. Quinquevalent arsenic ions and zinc ions do not interfere with lead determination. Under these conditions quinquevalent antimony ions are partially reduced to the elemental state. Antimony is separated from lead by treating the precipitate of the latter with a 0.2 N sulfuric acid solution of potassium dichromate. The gravimetric method gives satisfactory results for lead concentrations down to 1 mg/liter.

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PHOTOMETRIC DETERMINATION OF RHENIUM WITH DIETHYLDITHIOPHOSPHORIC ACID

A. I. Lazarev and V. V. Rodzaevskii
Akmolinsk Agricultural Institute

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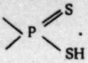
Septivalent rhenium is determined gravimetrically after precipitation by strong organic bases containing N, P, and As. Colored reagents of this type such as methyl violet, methylene blue, rhodamine B, and its esters, have been used for the photometric determination of rhenium. Stannous chloride is the best known and most widely used reagent for rhenium compounds in which the rhenium valence is less than seven, and which are normally prepared by reduction of septivalent rhenium compounds. Almost all the reagents of this group contain N and S in various combinations.

The combination of P and S atoms in a reagent molecule has not yet been examined with respect to rhenium; accordingly, we have examined the interaction of diethyldithiophosphoric acid with rhenium compounds.

This reagent contains the atomic group  .

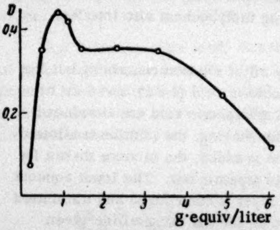


Fig. 1. Relation between the color intensity of the benzene layer and acid concentration.

Diethyldithiophosphoric acid has been used for the detection and determination of molybdenum [1, 2], cadmium, copper, palladium, etc [3]. There is a published reference to the interaction of rhenium with diethyldithiophosphoric acid [3].

Our experiments have shown that in acid media at room temperature, diethyldithiophosphoric acid does not react with septivalent rhenium compounds. When such a solution is heated to boiling, a colored compound is formed. Bearing in mind that diethyldithiophosphoric acid possesses reducing properties [4], we assumed that reduction of the perrhenate ion occurs on heating. We decided that it would be interesting to study this reaction in the presence of a reducing agent, and we chose stannous chloride. Addition of stannous chloride to a mixture of solutions of potassium perrhenate, diethyldithiophosphoric acid, and hydrochloric acid led to the formation of an orange colored compound which was sparingly soluble in aqueous solutions. The compound obtained was soluble in organic solvents.

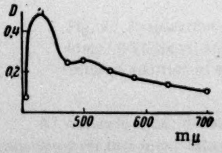


Fig. 2. Absorption curve of a benzene solution.

The reaction conditions were studied photometrically on a FÉK-M photoelectrocolorimeter of the Lang type. Formation of the complex is complete in 10 min; the colored compound can then be extracted with organic solvents.

The complex is stable at hydrochloric acid concentrations of 1-3

TABLE 1

Molar Extinction Coefficients (at 436 mμ)

Solvent	Molar extinction coefficient
Chloroform	$2.8 \cdot 10^2$
Diethyl ether	$4.4 \cdot 10^2$
Ethyl acetate	$5.4 \cdot 10^2$
Benzene	$6.2 \cdot 10^2$
Isobutanol	$6.3 \cdot 10^2$
Isoamyl acetate	$7.7 \cdot 10^2$

TABLE 2

Determination of Rhenium in Pure Solutions

Potassium perrhenate, mg						Mean square deviation, ± %
taken	found					
3,84	3,76;	3,76;	3,80;	3,91;	3,93	1,9
2,56	2,42;	2,48;	2,50;	2,60;	2,64	3,7
1,92	1,80;	1,81;	1,82;	1,92;	1,92	2,7
1,28	1,28;	1,28;	1,28;	1,30;	1,30	0,7
0,64	0,62;	0,63;	0,64;	0,64:	0,66	2,7

equiv./liter (Fig. 1). We carried out experiments in hydrochloric acid of about 1 N.

The optimum concentration of diethyldithiophosphoric acid is 0.2%, while that of the stannous chloride is 0.5%.

The absorption curve of a benzene extract, which was obtained on a Lange type photocolorimeter, shows that maximum absorption occurs at 436 mμ (Fig. 2).

The molar extinction coefficients of solutions of the compound of rhenium with diethyldithiophosphoric acid are given in Table 1; these values show that benzene is the most suitable solvent.

The relation between rhenium concentration and the optical density of benzene solutions is not linear (Fig. 3).

The mean square deviation, found from a small number of observations [5], does not exceed ± 4%.

Cupric ions in amounts greater than 0.2 mg in the test solut interfere with the reaction; 0.6 mg arsenic, 2 mg ferric ions, less than 0.1 mg of antimony, and 0.01 mg molybdenum also interfere. One determination takes 15-20 min.

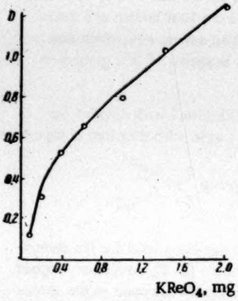


Fig. 3. The relation between optical density and rhenium concentration.

Analytical Procedure. Twenty ml of solution containing not less than 0.1 mg rhenium, 5 ml of hydrochloric acid (1 : 1), and 6 ml of a 1% aqueous solution of diethyldithiophosphoric acid are introduced into a 100 ml separating funnel. After shaking, the solution is allowed to stand for 10 min, 10 ml of benzene is added, the mixture shaken for one minute, and the layers allowed to separate out. The lower aqueous layer is run off. The upper benzene layer is centrifuged and transferred to a cuvette with a layer thickness of 30 mm. The optical density is measured at 436 mμ using a blue-green filter. Benzene is used as the reference solution. The rhenium content is determined from a calibration curve.

SUMMARY

Conditions have been established for the extraction photometric determination of rhenium using diethyldithiophosphoric acid.

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SPECTROCHEMICAL DETERMINATION OF SMALL AMOUNTS OF ALUMINUM AND SILICON IN NIOBIUM PENTOXIDE

T. M. Moroshkina and G. F. Malinin

A. A. Zhdanov Leningrad State University

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Several articles have been published in recent years on the spectrographic determination of impurities in niobium [1-3]. We are unaware, however, of any papers dealing with the determination of small amounts of aluminum and silicon.

Determination of less than 0.01 % of aluminum and silicon in niobium pentoxide is bound up with several difficulties: non-availability of sufficiently pure electrodes, the need for using special vessels, etc. In addition, the niobium spectrum has a complex structure and it is difficult to distinguish weak spectral lines of impurities on its background. In order to increase the sensitivity of impurity determination, we used the method of fractional distillation of samples with a carrier. Conditions can be chosen such that most of the aluminum and silicon present as impurities can be evaporated before the bulk of the niobium starts to evaporate. Use of a carrier ensures that the intensity of the impurity lines is increased. We tested Na_2CO_3, $CuCl_2$, Cu_2Cl_2 and AgCl as carriers. Cu_2Cl_2 and AgCl gave the best results, but cuprous chloride is comparatively unstable and is not very convenient to use.

AgCl was therefore used. Evaporation curves of the impurities and of niobium, with and without addition of silver chloride, are shown in Figs. 1 and 2. Addition of AgCl enhanced the fractionation effect. The boiling point of silver chloride is low (1550°). It is evident that AgCl, on evaporation, lowers the temperature of the spectrum excitation course, and this temperature is insufficient for intense evaporation of the slightly volatile niobium pentoxide.

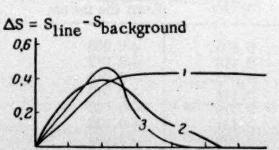

Fig. 1. Evaporation curves of (1) niobium, (2) silicon, and (3) aluminum without addition of silver chloride.

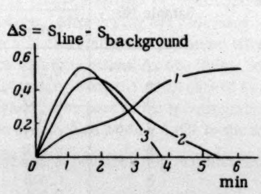

Fig. 2. Evaporation curves of (1) niobium, (2) silicon, and (3) aluminum with addition of silver chloride.

At the same time, the aluminum is chlorinated, and the readily volatile chloride is almost completely evaporated off in 2 min. Silicon is not chlorinated under these conditions, but the volatility of silicon is sufficient for most of it to evaporate before the niobium pentoxide starts to pass into the arc flame.

TABLE 1

Sample No.	Al content, %		Relative error, %	Si content, %		Relative error, %
	added	found		added	found	
1	0,001	0,00087	−13,0	0,005	0,0062	+24,0
2	0,0045	0,00523	+16,2	0,009	0,0105	+16,7
3	0,008	0,0092	+15,0	0,025	0,0257	+2,8
4	0,015	0,0155	+3,3	0,045	0,0501	+11,3
5	0,020	0,0224	+12,0	0,070	0,0617	−11,9
6	0,05	0,0462	−7,8	0,10	0,0960	−4
7	0,10	0,098	−2,0			
		Mean	±10			±12

TABLE 2

Sample No.	Al, 0,1 %		Al 0,001 %	
	I_{Al}/I_{Nb}	deviation from the mean	I_{Al}/I_{Nb}	deviation from the mean
1	0,536	+0,134	0,081	+0,002
2	0,412	+0,010	0,062	−0,017
3	0,338	−0,064	0,087	+0,008
4	0,366	−0,036	0,051	−0,028
5	0,320	−0,084	0,113	+0,034
6	0,442	+0,030	0,084	+0,005
7	0,403	+0,001	0,075	−0,004
8	0,398	−0,004	0,070	−0,009
9	0,395	−0,007	0,087	+0,008
10	0,412	+0,010	—	—
Mean Reproducibility	0,402	±0,048 ±12 %	Mean 0.079 Reproducibility	±0,013 ±17 %

TABLE 3

Sample No.	Si 0,1%		Si 0,005%	
	I_{Si}/I_{Nb}	deviation from the mean	I_{Si}/I_{Nb}	deviation from the mean
1	0,340	−0,036	0,105	+0,006
2	0,405	+0,029	0,116	+0,017
3	0,347	−0,029	0,083	−0,016
4	0,381	+0,005	0,118	+0,019
5	0,291	−0,085	0,079	−0,020
6	0,372	−0,004	0,121	+0,022
7	0,401	+0,025	0,090	−0,009
8	0,415	+0,039	0,089	−0,010
9	0,395	+0,019	0,075	−0,024
10	0,413	+0,037	0,114	+0,015
Mean	0,376	±0,031	Mean 0.099	±0,0158
Reproducibility		±8,3%	Reproducibility	±159%

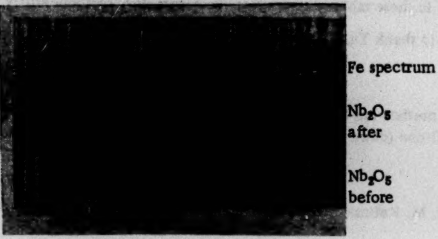

Fig. 3. Partial spectra of Nb_2O_5 before and after purification from silicon.

Determinations were carried out on a Hilger autocollimating spectrograph. An ac arc supplied by a DG-1 generator (18 amp at a voltage of 220 v) served as the light source. The spectrograph slit was 0.015 mm. The carbon electrodes had a diameter d = 6 mm. Samples were placed in a crater in the lower electrode, the crater was 3 mm deep and 3.5 mm in diameter. The upper electrode was sharpened to a truncated cone with an area of 1 mm. The inter-electrode gap was 3 mm.

The analytical lines were Al 3082.16 and Si 2881.58. The reference lines were Nb 3097.12 for aluminum, and Nb 2884.972 for silicon.

Exposure time was 2 min. A curve which was constructed within the coordinates log I/I_2 and log C [4] was used for the work. The background was taken into account. Platinum and stainless steel vessels replaced the glass and porcelain vessels when silicon was determined. The purity of the carbon electrodes was checked and the work was carried out with electrodes free from silicon and aluminum. In order to prepare standards, ordinary reagent grade niobium pentoxide was purified from aluminum by differential hydrolysis [5], the first fraction, which was almost free from aluminum, being taken. Niobium pentoxide was purified from silicon by dissolving an aliquot of the former in hydrofluoric acid and evaporating off the silicon as SiF_4. Part of the niobium pentoxide spectrum before and after purification from silicon is shown in Fig. 3.

Standards were prepared by adding a known amount of standard solutions of $Al_2(SO_4)_3 \cdot 16H_2O$ or $Na_2SiO_3 \cdot 9H_2O$ to an accurately weighed aliquot of spectrographically pure niobium pentoxide. After drying and calcining, the sample was mixed with a known amount of powdered silver chloride. The mixture was carefully mixed for one hour. Standards were prepared containing from 0.1 to 0.005% of Si and Al. The ratio $Nb_2O_5 \cdot AgCl = 2 : 1$. Twenty or 40 mg samples were taken. The part of the spectrogram shown in Fig. 4 gives an idea of the enhanced sensitivity of the aluminum line obtained on adding AgCl to the sample.

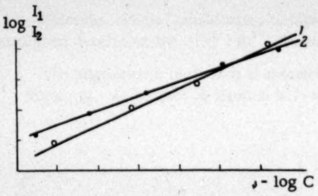

Fig. 4. Calibration curve (1) for silicon determination, (2) for aluminum determination.

Calibration curves were constructed on the basis of the standards prepared (Fig. 4), and silicon and aluminum were then determined in a series of samples.

Table 1 contains results for the spectrographic determination of silicon and aluminum in niobium pentoxide.

These results show that during the determination of small amounts of aluminum (0.001%) and silicon (0.005%), the mean relative experimental error is not greater than ±10% for aluminum and ±12% for silicon.

Tables 2 and 3 contain results which characterize the reproducibilities of the relative intensities for two samples, each of which was photographed ten times, the lowest determinable concentrations of the two elements being taken.

The results given in these tables demonstrate the satisfactory reproducibility of the relative intensities.

The authors wish to thank Yu. V. Morachevskii for his advice and help in the work described here.

SUMMARY

A spectrographic method has been developed for the direct determination of small amounts of aluminum (down to 0.001%) and silicon (down to 0.005%) in niobium pentoxide; the experimental error is ± 12%.

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PHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH XYLENOL ORANGE

V. F. Luk'yanov and E. M. Knyazeva

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Xylenol orange is widely used at present as a complexometric indicator for the titration of many elements including zirconium [1]. Recently the use of xylenol orange for the photometric determination of zirconium and hafnium was described [2, 3]. We have used xylenol orange for the determination of zirconium in ores, the technique we used being considerably more simple than that suggested by Cheng [2, 3]. In 0.2-1 N hydrochloric acid, xylenol orange forms a red compound with zirconium ions (λ_{max} = 540 mμ). Absorption curves of the reagent and of its compound with zirconium are shown in Fig. 1. The zirconium compound forms almost instantaneously and is stable for several days. The photometric method involving xylenol orange ensures results with the highest reproducibility. The reagent is no less sensitive and selective than alizarin S, arsenazo I, arsenazo II, and pyrocatechol violet. Table 1 contains the permissible amounts of foreign elements in a final volume of solution of 50 ml.

Chloride, nitrate, perchlorate, sulfate (up to 100 mg), and tartrate (up to 5 mg) ions do not interfere with zirconium determination. Cr^{3+}, Bi^{3+}, fluoride, and phosphate ions interfere.

The photometric method is characterized with the speed with which it can be carried out; it consists of following. An aliquot of solution is evaporated with 5 ml of distilled hydrochloric acid to a volume of about 1 ml. The solution is transferred from the beaker to a 50 ml standard flask, 0.5 ml of a 0.01 M (about 0.8%) aqueous solution of xylenol orange is added and the volume made up to the mark with 0.5 N hydrochloric acid. The optical density is measured in a FÉKN-57 photo colorimeter using a No. 5 filter (λ = 536 mμ) and cuvettes with a layer thickness of 20 mm.

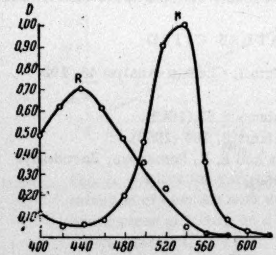

Fig. 1. Absorption curve of xylenol orange and of its complex with zirconium. R) $5 \cdot 10^{-5}$ M xylenol orange in 0.5 N HCl; K) $5 \cdot 10^{-5}$ M xylenol orange and $1 \cdot 10^{-4}$ M $ZrOCl_2$ in 0.5 N HCl; SF-4; cuvette 10 mm.

A calibration curve is constructed in the same way (Fig. 2).

Zirconium was determined in ores (Table 2) by the method described above.

Analytical Procedure. A 0.2-0.5 g aliquot of ore is fused with 5-10 g of sodium peroxide at 650° in a corundum crucible. The cooled melt is leached with hot water, and the liquid boiled for 5-10 min to destroy hydrogen peroxide (the volume of the solution should not be less than 250-300 ml). The solution is filtered through a fine filter (blue band) and the first portions of filtrate tested for absence of hydrogen peroxide (the filtrate is acidified with sulfuric acid and tested with Ti). The precipitate on the filter is washed 3-4 times with 5% sodium hydroxide, once or twice with water, and then dissolved in hot 2 N hydrochloric

TABLE 1

Effect of Various Elements on the Determination of Zirconium by Xylenol Orange (C_{Zr} = = 50 μg in 50 ml)

Elements	Permissible amount, μg/50 ml	Ratio Zr : element	Elements	Permissible amount, μg/50 ml	Ratio Zr : element	Elements	Permissible amount, μg/50 ml	Ratio Zr : element
Fe^{3+}	50	1 : 1	Cu^{2+}	5000	1 : 100	Nd^{3+}	2000	1 : 40
Fe^{2+}	5000	1 : 100	Cd^{2+}	500	1 : 10	La^{3+}	1000	1 : 20
Al^{3+}	500	1 : 10	Cr^{3+}	50	1 : 1	TiO^{2+}	1000	1 : 20
Bi^{3+}	50	1 : 1	Pb^{2+}	5000	1 : 100	UO_2^{2+}	200	1 : 4
Ni^{2+}	200	1 : 4	Sn^{2+}	1000	1 : 20	WO_4^{2-}	1000	1 : 20
Co^{2+}	2000	1 : 4	Sn^{4+}	500	1 : 10	MoO_4^{2-}	1000	1 : 20
Zn^{2+}	1500	1 : 3				VO_3^-	2000	1 : 40

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* Reduced with 10 mg ascorbic acid.

TABLE 2

Determination of Zirconium in Ores

Zr found, %			Zr found, %		
with xylenol orange		with arsenazo III [4]	with xylenol orange		with arsenazo III [4]
0,050	0,052	0,054	0,33	0,33	0,28
0,060	0,061	0,058	0,33	0,32	0,30
0,075	0,076	0,074	0,050	0,050	0,042
0,42	0,42	0,46	0,055	0,055	0,057

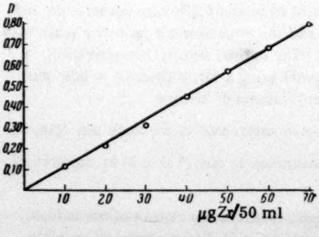

Fig. 2. Calibration curve for determination of zirconium with xylenol orange (20 mm cuvette).

acid. The solution is transferred to a 200-250 ml standard flask, and its volume made up to the mark with 2 N hydrochloric acid. An aliquot of this solution is taken (5 or 10 ml) and the procedure outlined above then followed.

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DETERMINATION OF SMALL AMOUNTS OF NIOBIUM IN ORES CONTAINING TITANIUM, TUNGSTEN, MOLYBDENUM, AND CHROMIUM*

V. M. Dorosh

Irkutsk Scientific-Research Institute of Rare Metals

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Good results are obtained when manganese dioxide is used as a collector for separating small amounts of niobium. This collector is used for the analysis of ores with a complex composition. The following analytical procedure is recommended. A 0.1-0.2 g aliquot (depending on the niobium content) is fused in a nickel or iron crucible with 5-10 g of sodium hydroxide. The melt is leached with water, the solution plus residue is boiled for 2-3 min and the residue filtered off on a fine filter and washed 3-5 times with 2% NaOH. The filtrate contains Cr, W, Mo, Sn, Si, and Al, while the residue contains Nb, Ta, Ti, and Fe. When the tungsten and chromium contents are high, the hydroxides are reprecipitated with sodium hydroxide. The filter plus residue, which has been washed with caustic solution, is wrapped round the edge of the beaker and the residue is washed off with a solution of sulfuric acid (2 : 250) to which several drops of hydrogen peroxide has been added; the filter is then discarded. Six to eight ml of sulfuric acid (1 :2) is added to the contents of the beaker and the whole boiled to destroy H_2O_2. One ml of 1 N manganese sulfate is added to the cooled solution, followed by 2 g of ammonium or potassium persulfate. The volume of the solution should be about 200 ml. The beaker is placed on a hot plate.

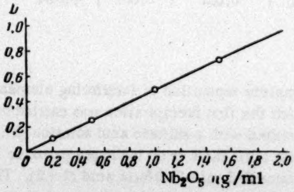

Fig. 1. Calibration curve for determination of niobium with thiocyanate and acetone at 360 mμ in a cuvette with a layer thickness of 3 cm.

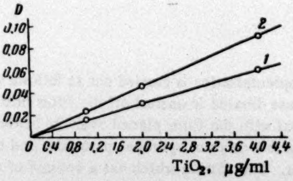

Fig. 2. Correction curve for titanium during determination of niobium. 1) Titanium with thiocyanate and acetone; 2) titanium with hydrogen peroxide (360 mμ, cuvette 3 cm).

The solution plus deposited manganese dioxide is boiled for 7-10 min, and, after being allowed to stand for some time, the precipitate is filtered off through a small fine filter and washed with dilute sulfuric acid (2 : 250). The filtrate contains Mo, Ti, Cr, Zr, and Fe. The niobium is isolated quantitatively with the manganese dioxide [1].

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* Read at the conference on the analysis of rare and semiconducting elements held in Moscow, December 8, 1959.

TABLE 1

Comparative Results for the Determination of Niobium by Various Methods (%)

Test material	Chemical methods of analysis		Physical methods of analysis	
	recom. MnO_2 method	Bykov's method	spectrographically	x-ray spectrographically
Columbite ore	0,006	0,005	0,004	0,007
" "	0,028	0,027	0,026	0,027
" "	0,009	0,009	0,009	0,011
" "	0,020	0,020	0,020	0.022
" "	0,013	0,012	0,012	0,013
" "	0,009	0,008	0,008	0,010
" "	0,005	0,005	0,005	0,005
" "	0,060	0,060	0,060	0,080
Zirconium ore	0,110	0,110	0,110	0,150
Eudialite ore	0,250	0,250	0,250	0,300
Pyrochlore ore	0,345	0,350	0,350	0,340
Concentrate from columbite ore	0,480	0,480	0,500	0,520
Concentrate from pyrochlore ore	0,760	0,780	0,800	0,840
" " " " "	1,970	2,000	2,250	2,000

TABLE 2

Determination of Niobium in the Presence of Tungsten and Molybdenum

Nb_2O_5 content (mean 5 repeat determinations)	WO_3 added		Mo added		Nb_2O_5 found by the recommended method, %	Deviation from the mean arithmetic value, %	
	mg	ratio $Nb_2O_5:WO_3$	mg	ratio $Nb_2O_5:Mo$		absolute	relative
0,027	9,37	1 ; 69	8,5	1 : 63	0,026	0,001	—3,71
0,033	9,37	1 : 56	8,5	1 : 51	0,031	0,002	—6,03
0,031	9,37	1 : 60	8,5	1 : 55	0,030	0,001	—3,55
0,031	9,37	1 : 60	8,5	1 : 55	0,030	0,001	—3,55
0,029	9,37	1 : 64	8,5	1 : 58	0,030	0,001	+3,44
0,026	9,37	1 : 74	8,5	1 : 65	0,027	0,001	+3,84

Reprecipitation is carried out as follows to effect more complete separation of interfering elements. The manganese dioxide is washed off the filter into the beaker in which the first precipitation was carried out, and the funnel with the filter placed over the beaker. The filter is washed with a sulfuric acid solution (2 : 250) containing a few drops of hydrogen peroxide, and then with pure water until there is no hydrogen peroxide left on the filter. The filtrate which has a volume of about 200 ml contains 6-8 ml of sulfuric acid (1 : 2). The filter is used for the next filtration. The solution is boiled to destroy hydrogen peroxide, it is then cooled, and precipitation with persulfate repeated as described above.

The manganese dioxide precipitate containing the entrained niobium is fused with 1.5-3 g of sodium bisulfate. After cooling, the melt is dissolved in 15% tartaric acid solution and the volume made up to 25 or 50 ml. The final tartaric acid concentration is 7.5%.

Niobium is determined photometrically by Freund and Levitt's method [2], in an acetone–water medium with thiocyanate at 360 mμ (filter No. 1, FEK-N photocolorimeter) using a 3 cm cuvette. The niobium content is calculated by means of a calibration curve (Fig. 1). If titanium has not been completely removed, a correction obtained from a curve (Fig. 2) is applied.

The thiocyanate method for niobium [3] is very sensitive. In the case of a 2 g aliquot of ore containing 0.005% Nb_2O_5, and a dilution of 25 ml, a 10 ml aliquot contains 0.04 mg Nb_2O_5. A solution with a volume of 50 ml (0.8 μg/ml) has an optical density of 0.4. Accordingly, a 5 ml aliquot can be used for a determination. By increasing the weight taken to 5 g, the sensitivity is increased and it is possible to determine thousandths of a percent. Table 1 contains the results of niobium determinations.

For determination of niobium in samples of columbite and zirconium ores by physical methods, an enrichment technique was used beforehand (enrichment factor $K_{enrich.}$ = 30-50). No enrichment was used for the other ores.

The analytical method including alkali decomposition and precipitation of niobium in a sulfuric acid medium is suitable for ores containing tungsten, molybdenum, and chromium. In order to confirm this, a known amount of tungsten and molybdenum concentrates was added before fusion to an aliquot of ore (0.5 g) with a known niobium content. After two precipitations with MnO_2, the niobium was determined by the thiocyanate method. As Table 2 shows, the results obtained for niobium are in complete agreement with the results obtained for these sample before addition of tungsten and molybdenum.

SUMMARY

During analysis of ores containing titanium, tungsten, molybdenum, and chromium, small amounts of niobium are separated by coprecipitation with manganese dioxide. A photometric thiocyanate finish is used for determining the niobium.

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DETERMINATION OF PALLADIUM AND NICKEL, AND OF PALLADIUM AND COPPER IN EACH OTHERS PRESENCE

A. S. Pesis

Perm State Medical Institute

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Previous papers have dealt with formation of compounds between β-hydroxynaphthaldehyde and palladium and other divalent cations [1], and with the quantitative determination of palladium with this aldehyde in the presence of a number of cations [2]. Since β-hydroxynaphthaldehyde precipitates palladium in acid media (pH 2.5-3), while it precipitates copper and nickel at pH > 7, it should be possible to determine palladium simultaneously with one of these elements without preliminary separation. The classical dimethylglyoxime method only permits determination of palladium and nickel. Determination of copper by this aldehyde has been described previously [3]; nickel has not been precipitated quantitatively by β-hydroxynaphthaldehyde.

Experimental. Palladium nitrate was prepared by dissolving an accurately weighed aliquot of palladium wire (0.1 g) in 2-3 ml concentrated HNO_3, sp. gr. 1.43. Nickel and cupric nitrates were prepared by dissolving accurately weighed aliquots of the pure metals (0.2 g) in 2 ml HNO_3, sp. gr. 1.39. The solutions were transferred to standard flasks and made up to the mark with water.

β-Hydroxynaphthaldehyde was synthesized from β-naphthol and chloroform in an alcoholic-alkali medium; it was distilled under vacuum and recrystallized from alcohol; m. p. 80-81° [4].

Determination of Palladium and Nickel. Five ml of palladium nitrate solution and 10 ml of nickel nitrate solution pH 2.5-3 are mixed. The mixture is diluted with an equal volume of alcohol. Palladium is precipitated with 5 ml of a 1% alcoholic solution of the reagent. On mixing with a rod, a yellow precipitate separates out. The latter is allowed to stand for 20-25 min at room temperature, it is then kept for 5 min on a water bath at 70°; it is next filtered off through a Schott No. 2 crucible, washed with 50% alcohol and dried at 110° for 25-30 min. The filtrate is quantitatively transferred from the Bunsen flask to a beaker; to the latter is added a few drops of 0.25 N sodium hydroxide, and crystalline sodium acetate added to adjust the pH to 7.2-7.5, the liquid brought up to the boil, and precipitation effect by addition of 10 ml of heated 1% alcoholic solution of the reagent. The yellow-green precipitate is allowed to stand for 25 min, filtered through a Schott No. 4 crucible, washed with 50% alcohol, and dried at 150° for 40-45 min. The conversion factor to palladium is 0.2377, while the conversion factor to nickel is 0.1464.

Palladium and copper are determined in a similar way in a solution containing both elements. After filtering off the palladium precipitate, the pH is increased by adding small amounts of 0.25 N NaOH and sodium acetate, or by adding ammonium hydroxide as described earlier [3]. The use of dilute alkali and sodium acetate for adjusting the pH to 7.3-7.5 has the advantage that the solutions do not darken. On the other hand care must be taken during neutralization in order to avoid formation of hydroxides.

As the results given in Tables 1 and 2 show, the experimental errors do not exceed the permissible values.

TABLE 1

(5.00 mg Pd taken)

Taken, mg	Found, mg		Absolute error, mg	
Ni	Pd	Ni	for Pd	for Ni
10,00	5,10	10,25	+0,1	+0,25
10,00	5,00	10,20	0,00	+0,20
5,00	4,90	5,00	−0,10	0,00
10,00	5,20	9,88	+0,20	−0,12
9,83	5,10	9,80	+0,10	−0,03

TABLE 2

(5.00 mg Pd taken)

Taken, mg	Found, mg		Absolute error, mg	
Cu	Pd	Cu	for Pd	for Cu
5,00	4,90	5,10	−0,10	+0,1
10,00	5,10	10,2	+0,10	+0,2
5,00	5,00	5,16	0,00	+0,16
10,00	5,00	9,90	0,00	−0,1

SUMMARY

A method is suggested for the determination of palladium and nickel, and of palladium and copper on one aliquot. Palladium is precipitated with β-hydroxynaphthaldehyde at pH 2.5-3, while nickel and copper are precipitated at pH 7.2-7.5.

LITERATURE CITED

1. **V. I. Kumov, Z. A. Bitovt, and A. S. Pesis, Zhur. Neorg. Khim. 3, 1181 (1958).**
2. **A. S. Pesis and Z. A. Bitoft, Zhur. Anal. Khim. 15, 200 (1960).**
3. **S. I. Gusev and V. I. Kumov, Zhur. Anal. Khim. 15, 303 (1956).**
4. **Synthesis of Organic Preparations, 3 [Russian translation] (IL, Moscow, 1952), p. 365.**

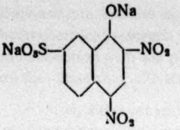
THE USE OF NAPHTHOL YELLOW INSTEAD OF URANYL NITRATE IN THE STANDARD METHOD OF DETERMINING THE OXIDIZABILITY OF COMMERCIAL ETHANOL

I. S. Mustafin and N. K. Memkova

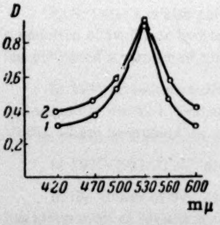
Saratov State University

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
p. 255, March-April, 1961
Original article submitted

The oxidizability of commercial ethanol produced by fermentation is determined, according to GOST 5964-51, by comparing its color after adding a known amount of potassium permanganate solution to it, with the color of a standard solution for preparation of which uranyl nitrate is used.

Uranyl nitrate can be replaced by naphthol yellow which is more readily available; this reagent,  , is commercially produced in the USSR. The dye is readily soluble in water, and its solutions are stable and chemically inert and have a yellow color in the pH range 1 to 13.

Aqueous solutions of uranyl nitrate and naphthol yellow have similar absorption curves, and their maxima are located at the violet edge of the visible part of the spectrum. At the same time, the absorption intensity of naphthol yellow solution is three orders higher (2.4×10^3) than that of isomolar solutions of uranyl nitrate. From these results it is possible to calculate the naphthol yellow concentration for which its solutions will have equal optical density to that of uranyl nitrate in the standard solution; we found that the requisite concentration is 3×10^{-5} M.



Absorption curves of standard solutions. 1) Uranyl nitrate + + $CoCl_2$; 2) naphthol yellow + + $CoCl_2$.

Preparation of a standard solution containing naphthol yellow instead of uranyl nitrate reduces to mixing 5 ml of the first solution with 7 ml of the second solution, and making up the volume to 100 ml with distilled water.

First Solution. fifty g of pure cobalt chloride is dissolved in a one liter standard flask; second solution, 0.0118 g of naphthol yellow is dissolved in a one liter standard flask.

Absorption curves for a solution prepared exactly as specified in GOST (Curve 1) and for a solution in which uranyl nitrate is replaced by naphthol yellow (Curve 2) are shown in the Fig. They clearly show the identity of the light absorption of standard solutions prepared from uranyl nitrate and naphthol yellow.

Standard solutions prepared with this dye are stable with time; the optical density hardly changes at all in the course of 20-25 days.

An attempt to use the standard technique for determining the oxidizability of alcohol from the Saratov synthetic alcohol plant proved unsuccessful: on adding potassium permanganate to the test alcohol solution the solution immediately became brown; this indicates the presence of a large amount of readily oxidizable materials in the synthetic alcohol.

SUMMARY

It has been shown that naphthol yellow can be used instead of uranyl nitrate for preparing the standard solution used for determining the oxidizability of alcohol.

PETR NIKOLAEVICH PALEI

(On his sixtieth birthday)

On October 19, 1960,Petr Nikolaevich Palei,one of our outstanding analytical chemists,celebrated his sixtieth birhday.

P. N. Palei was born October 19, 1900 in Zhitomir in the Ukraine. While still student in Leningrad State University,in 1922,he taught chemistry in the Artillery Pyrotechnical School, and started,in 1924,to carry out hydrochemical research using the new—at that time—colorimetric and electrometric methods of determining pH, in connection with the photochemical activity of plants. From 1926 he also worked in the Geological Committee on the Chemistry of Natural Water

P. N. Palei set up new types of field hydrochemical laboratories and established the chemical composition of water from many sources in the USSR. From 1929 to 1937 he was the head of the hydrochemical laboratory of the All-Union Institute of Health Resort Administration. Among the numerous hydrochemical researches of P. N. Palei, particular mention should be made of his work on the study of the hydrogen sulfide water of Psekuns and Matsesta, the mineral waters of Osetni, Dagestan, Kareliya, the Far East, and the Ural, on the geochemistry of lake loam from Trans Ural, Crimea, and the Far Eastern Region, as well as his work on the escape of hydrogen sulfide from Matsesta water, and his studies on sulfide-carbonate equilibria.

P. N. Palei has also published a number of papers on balneotherapy; a method which he developed for the production of synthetic hydrogen sulfide water has been adopted in the health resorts of the Soviet Union. He has published a number of textbooks on field hydrochemical analysis.

In 1937 he switched over to work in the Biogeochemical Laboratory of the Academy of Sciences, USSR (subsequently the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR), where he studied the distribution of rare and dispersed elements in mineral waters.

In 1937-1939 P. N. Palei developed methods for the determination of small amounts of beryllium.

In the course of the last 15 years, working in the Institute of Geochemistry and Analytical Chemistry, he has given most of his attention to improving, developing, and introducing new precision methods of analysis into practice. At the same time,he has also carried out a thorough and systematic study of the analytical chemistry of the actinides.

He has published more than 200 papers. He maintains a close connection with many industrial laboratories and enterprises and gives them his help. He has instructed a large number of young scientists, particularly in precision methods of analysis and in the analytical chemistry of the actinides. He also carries out social duties, being a member of the Commission on Analytical Chemistry. He has been awarded prizes for his fruitful work.

The Commission on Analytical Chemistry, the Editorial Board of the Journal of Analytical Chemistry, analytical chemists, his co-workers, and students wish to congratulate him on his many years of fruitful scientific work.

NEW REAGENT FOR THE LUMINESCENT DETERMINATION OF MAGNESIUM

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
inside back cover.

The All-Union Scientific-Research Institute of Chemical Reagents (IREA) has synthesized a new reagent for the luminescent determination of magnesium; this reagent – lumomagneson – permits determination of 0.02 μg Mg in 5 ml in an aqueous medium at pH 10.0. Equal amounts of foreign cations do not interfere with magnesium determination. The permissible ratio of Mg : Ca = 1 : 100.

Organizations and enterprises wishing to test the new reagent can get a free sample and instructions for its use by sending a request to the following address: Moscow, Samokatnaya Ulitsa, Dom 4a – Institute of Chemical Reagents.

Lumomagneson is not being produced on the plant scale at the moment, and in order to decide whether it is worth producing on a commercial scale, the Institute of Chemical Reagents earnestly requests all organizations and enterprises to let them know two months from receipt of samples what they think of its practical value.

The Institute will give advice on all problems connected with the use of lumomagneson.

A CONFERENCE ON EXTRACTION IN ANALYTICAL CHEMISTRY

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
back cover.

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, and the Commission on Analytical Chemistry intend to convene a conference on extraction in analytical chemistry, in Moscow in December 1961.

The conference will discuss reports on the use of extraction in analytical chemistry, in particular, on the following lines:

1. Theoretical questions of extraction.

2. General methodological questions of the use of extraction in analytical chemistry (new principles of extraction separation, extraction–photometric method, the study of complex formation by extraction methods, and the use of extraction in radiochemical analysis).

3. The application of extraction methods for the analysis of various materials.

4. New extractants and extraction apparatus.

5. Questions relating to the classification and terminology of extractions processes and methods.

The Institute of Geochemistry and Analytical Chemistry, and the Commission on Analytical Chemistry invite workers in scientific-research institutes, universities, and industrial laboratories to take part in the work of the conference.

Titles and annotated reports (1-2 typewritten sheets) as well as requests for tickets to attend the conference should be sent to the organizing committee of the conference before July 15, 1961 at the following address: Moscow, V-133, Vorob'ev Road, 47a, Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Organizing Committee on Extraction.

The exact date of the conference will be announced later.

Organizing Committee

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE		TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN		
					Vol.	Issue	Year
AÉ	Atomnaya énergiya		Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal		Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki		Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal		Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka		Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika		Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika		Biophysics	National Institutes of Health*		1	1957
	Biokhimiya		Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny		Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR		The translation of this journal is published in sections, as follows:				
		Life Sciences	Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
			Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
			Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
			Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
			Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences	Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
			Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1 6	1957-1958
			Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1 6	1957-1958
		Mathematics	Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics	Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
			Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'		Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz		Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie		Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya		Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie		Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova		Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii		Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya		Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela		Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika		Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (In English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics—JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics—Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

THE INCREASE IN THE RADIATION INTENSITY OF METALS IN A FLAME AS A RESULT OF IONIZATION SUPPRESSION

N. S. Poluéktov and R. A. Vitkun
Institute of General and Inorganic Chemistry,
Academy of Sciences Ukr.SSR, Odessa Laboratory

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pp. 260-267, May-June, 1961
Original article submitted April 14, 1960

It is well known that when the vapors of two or more alkali metals which have low ionization potentials (K, Rb, Cs) are introduced into a flame, the radiation intensity of each of them increases to a value which is greater than when only one metal is present [1-2]. This phenomenon which is used for increasing the sensitivity of Cs determination [3-5] is explained by ionization suppression [6-11]. When the flame temperature is high enough, metal atoms which are formed as a result of thermal dissociation of the salts introduced are partially ionized in accordance with the equation $Me \rightleftharpoons Me^+ + e^-$ (e^- is an electron). As a result, the partial pressure of the neutral atoms of the metal, which are responsible for the radiation of the resonance lines of the metal, is lower than the value to be expected in the absence of ionization. Addition of other ionizing metals which increase the partial pressure of the electrons in in the flame displaces the ionization equilibrium, while the partial pressure of the neutral atoms, and consequently the radiation intensity of their resonance lines connected with this, increases. At the same time there is a possibility of an interaction between the atoms of the test metal and atoms or radicals arising from the acid residue of the salt in the form of which the other metal is added, and a decrease, as a consequence of this, in the partial pressure of the atoms of the first metal (development of the anion effect). Nevertheless, in some cases (nitrates and hydroxides) this effect is negligibly small, and the resulting change in radiation intensity can be ascribed simply to the shift in ionization equilibrium. Hitherto no attempts have been made to develop theories which express the mutual effect of one ionizing metal on the radiation intensity of another in quantitative terms, using the hypothesis of the ionization of atoms as a basis.

Theory. First of all let us consider the ionization of one metal in a flame. The degree of ionization α_0, i.e., the ratio of the partial pressure of the ions P_{Me^+} to the total partial pressure P_N of the ions and nonionized metal ions P_{Me} introduced into the flame ($P_M = P_{Me} + P_{Me^+}$) can be calculated as follows. According to the ionization equation

$$\frac{P_{Me^+} \cdot P_{e^-}}{P_{Me}} = K_{ion}, \tag{1}$$

where P_{e^-} is the partial pressure of the electrons, K_{ion} is the ionization constant of the metal determined from the relationship:

$$\lg K_{ion} = -\frac{23053 \dot{I}}{4{,}573 T} + \frac{5}{2} \lg T - 6{,}49 + \lg \frac{g_{Me^+} \cdot g_{e^-}}{g_{Me}},$$

where $\dot{I}$ is the ionization potential of the atoms, ev; T is the flame temperature; g_{Me^+}, g_{e^-}, g_{Me} are the statistical weights of the ions, electrons, and neutral atoms. In the case of one metal $P_{e^-} = P_{Me^+}$. Substituting in equation (1) this value P_{e^-} and the values $P_{Me} = P_N - P_{Me^+}$, we get

$$\frac{(P_{Me^+})^2}{P_N - P_{Me^+}} = K_{ion}, \tag{2}$$

from which

$$\alpha_0 = \frac{P_{Me^+}}{P_N} = \frac{\sqrt{4a+1} - 1}{2a}, \tag{3}$$

where

$$a = P_N / K_{ion}.$$

Thus the degree of ionization α_0 for various atoms depends only on the ratio of the total partial pressure of the metal atoms introduced into the flame to the ionization constant. Fig. 1 shows the relation between the value of P_{Me^+}/P_N (in %) and the logarithm of the ratio P_N/K_{ion}. It is clear from the figure that the degree of ionization α_0 approaches zero for $P_N/K_{ion} > 1000$ [$\lg(P_N/K_{ion}) > 3$] and approximates to 100% for $P_N/K_{ion} < 0.01$ [$\lg(P_N/K_{ion}) < -2$].

It was interesting to establish the values of the degree of ionization for various real conditions by flame photometry. The total partial pressure of the metal atoms and ions in the gas flame depends on the concentration of metal salt in solution (C,M), the efficiency of the sprayer, the type of gas, amount of gas supplied to the burner in unit time, the temperature of the flame, and also on the extent to which the atoms and ions are combined as gaseous hydroxide molecules. Under the conditions used in the present work [12], the following relationships hold for the total partial pressure of the metal atoms which would be in the flame if there was no ionization, and if no molecules of gaseous hydroxides were formed:

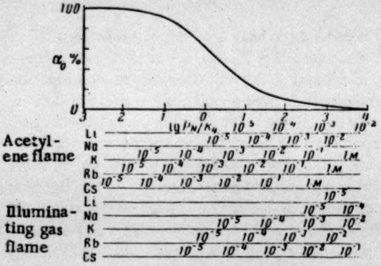

Fig. 1. Degree of ionization α_0 (in %) as a function of the log of the ratio P_N/K_{ion}. The values of the concentration of alkali metals in solution (M) are given under the curve for an acetvlene flame and for illuminating gas flame; these values correspond to definite values. of P_N/K_{ion} in the flame.

$$P_{N'} = C\cdot 10^{-3.7}\,a\,T \text{ (acetvlene flame)} \qquad (4)$$

$$P_{N'} = C\cdot 10^{-3.78}\,a\,T \text{ (illuminating gas flame)} \qquad (5)$$

These relationships were derived on the assumption that the concentration of metal atoms in the flame [13] $[N_{total}] = 6.2\cdot 10^{14}\cdot C$ atoms/cm^3. The equilibrium of the formation of hydroxide molecules conforms to the equation

$$\frac{P_{Me}\cdot P_{OH}}{P_{MeOH}} = K_{dissoc.}$$

where P_{OH} and P_{MeOH} are the partial pressures of hydroxyl radicals and metal hydroxide, and $K_{dissoc.}$ is the dissociation content of the latter. At not very high salt concentrations, the value of P_{OH} is several times smaller than P_{Me} and P_{MeOH}, and can accordingly be assumed to be constant. From this:

$$\frac{P_{Me}}{P_{MeOH}} = \frac{K_{dissoc.}}{P_{OH}} = \text{const} \qquad (6)$$

while the following relation is also constant

$$\frac{P_{Me}}{P_{MeOH} + P_{Me}} = \frac{P_{Me}}{P_{N_{total}}} = \beta \qquad (7)$$

β, which is the extent of dissociation of alkali metal hydroxides, has been studied very little. For the flame of an acetylene-- air mixture $\beta = 1$ in the case of sodium, since it does not form a stable hydroxide. In the case of the remaining metals, the tendency to form stable hydroxides increases in the order K, Rb, Cs, Li. The value of β for K = 0.43 while for Li $\beta = 0.21$. It should be noted that the value of β does not differ strongly from 1 and can be left out in further discussion. As for the concentration of metal in solution, we used the relationships (4) and (5) and the values of K_{ion} from Sakh's formula (Table 1).

These results are given in Fig. 1. As the figure shows, for the case of lithium and sodium in an illuminating gas flame, the fraction of ionized atoms is small, and neutral atoms are present in the main. In the case of potassium, ionization should become observable even at low concentrations 10^{-4} - 10^{-5} M, while it should be appreciable for rubidium and cesium over the same concentration range. In an acetylene flame ionization should be high for K, Rb, and Cs over the concentration range normally used in analysis, and should be observable even for lithium over the concentration range 10^{-4} - 10^{-5} M. Nevertheless, in actual fact, a limit is set on the ionization of the metals at low concentrations by the presence in the flame gas of charged particles whose partial pressure for an acetylene—air mixture, according to [14], is about 3.6×10^{8} equal to approximately $10^{-7.45}$ atm, and according to our results about $10^{-8.5}$ atm. Since, according to expressions 4 and 5, a partial pressure of atoms P_N which is close to this value is created at $C = 10^{-4} - 10^{-5}$ M, it follows that the background of charged particles in the flame will prevent ionization of metal introduced into the flame when the metal concentration in solution is below 10^{-4} - 10^{-5} M, such concentrations not being normally used in analysis. These results relate to that part of the flame which is 10-20 mm above the inner cone; near the zone of primary combustion of hydrocarbon flames the background of charged particle is significantly higher [11] and may lead to complete supression of ionization of the alkali metal introduced into the flame [15].

TABLE 1. Values of the Logarithm of the Ionization Constant of the Alkali Metals in an Acetylene and in Illuminating Gas Flame

Metal	Logarithm of ionization constant		$\log P_N/K_{ion}$ for 1 M salt solutions	
	Illuminating gas flame, T= 1970° K	Acetylene flame, T= 2360° K	Illuminating gas flame	Acetylene flame
Lithium	−12.03	−9.52	8.25	5.32
Sodium	−11.38	−9.00	7.60	3.20
Potassium	− 9.33	−7.31	5.55	3.51
Rubidium	− 8.93	−6.96	5.15	3.16
Cesium	− 8.20	−6.35	4.42	2.55

Let us consider how the concentration of nonionized metal atoms in the flame, and the radiation intensity related to it, will increase in the presence of another metal which is capable of ionizing. In order to develop the theory further it will be expedient to introduce the concept of the maximum possible increase in radiation intensity A (in the absence of self-absorption) which occurs as a result of complete conversion of all the metal ions into neutral atoms. Thus,

$$A = P_N / P_{Me}$$

since

$$P_{Me}/P_N = 1 - P_{Me^+}/P_N, \tag{8}$$

then using the value of P_{Me^+}/P_N from (3) we find that:

$$\frac{P_N}{P_{Me}} = \frac{1}{1 - P_{Me^+}/P_N} = \frac{2a}{2a + 1 - \sqrt{4a+1}} = A. \tag{9}$$

The relation between log A and gP_N/K_{ion} calculated by means of this equation is shown in Fig. 2. The maximum possible increase in radiation intensity at $\alpha = 1000$ amounts in all to 0.03 (3%), while for $\alpha = 100$ it is 0.103 (10.3%), i.e., it is low. At $\alpha = 10$ it already amounts to 0.37, while at $\alpha = 1$ it is 2.62 (262%); further, it increases almost inversely proportionally to α, and amounts to 1000 at $\alpha = 0.001$.

Comparison with the scale for P_N/K_{ion} values as a function of the concentration C in solution, however, shows that in the case of an acetylene flame an appreciable increase can only be expected for three elements K, Rb, and Cs; in the case of Na and Li it is only possible (and then only to a small extent – an increase of 10-20%) at very low concentrations of the elements in solution – 10^{-4}M and lower. In an illuminating gas flame an increase may be manifested to a small extent in the case of K, Rb, and Cs at very low concentrations, while there will be no increase at all in the case of Li and Na. In this connection one should bear in mind what was said above about the effect of the ionization of the flame itself.

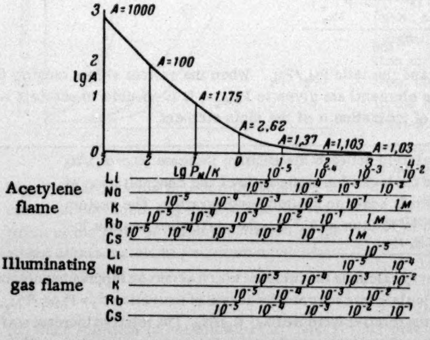

Fig. 2. The relations between the logarithm of the maximum possible increase A, following from ionization suppression, and the logarithm of the ratio P_N/K_{ion}. The concentrations of the alkali metals in solution (M) corresponding to definite values of P_N/K_{ion} in the flame are given under the curve.

When two metals Me_1 and Me_2 are present in the flame, the degree of ionization of each metal in the flame will be determined by three equations:

$$\frac{P_{Me_1^+} \cdot P_{e^-}}{P_{Me_1}} = K_{ion}, \tag{10a}$$

$$\frac{P_{Me_2^+} \cdot P_{e^-}}{P_{Me_2}} = K_{2\,ion}, \tag{10b}$$

$$P_{Me_1^+} + P_{Me_2^+} = P_{e^-}. \tag{10c}$$

In these equations P_{Me_1}, P_{Me_2}, $P_{Me_1^+}$, $P_{Me_2^+}$, P_{e^-} are the partial pressures of metal atoms, ions, and electrons, while K_{1ion} and K_{2ion} are the corresponding ionization constants. Using equations (10 a, b, c) it is possible to calculate the degree of ionization of each of the metals $\alpha = P_{Me^+}/P_N$ in the presence of the other in the flame, and from this, the relative increase as a fraction of the maximum, meaning by the latter the ratio of the increase in partial pressure of the atoms $(\alpha_0 - \alpha) \cdot P_N$ to the maximum possible $(\alpha_0 \cdot P_N)$.

In order to calculate the relative increase we substitute the value for P_e - from the equation (10c) in equations (10a) and (10b):

$$\frac{P_{Me_1^+} \cdot (P_{Me_1^+} + P_{Me_2^+})}{P_{Me_1}} = K_{1\,ion}, \tag{11a}$$

$$\frac{P_{Me_2^+} \cdot (P_{Me_1^+} + P_{Me_2^+})}{P_{Me_2}} = K_{2\,ion}. \tag{11b}$$

Having assigned definite value to $P_{Me_1^+}$ for definite values of $P_{N_1}/K_{1ion} = \alpha$, we calculate $P_{Me_2^+}$; for this purpose we substitute $P_{Me_1} = P_{N_1} - P_{Me_1^+}$ in equation (11a).

$$P_{Me_2^+} = \frac{a \cdot K_{1\,ion}^2}{P_{Me_1^+}} - K_{1\,ion} - P_{Me_1^+}.$$

Knowing $P_{Me_1^+}$ and $P_{Me_2^+}$, it is possible to determine P_{Me_2} from equation (11b):

$$P_{Me_2} = \frac{P_{Me_2} + (P_{Me_1^+} + P_{Me_2^+})}{K_{2\,ion}}.$$

It is then possible to calculate $P_{N_2} = P_{Me_2} + P_{Me_2^+}$ and the ratio P_{N_2}/P_{N_1}. When the various values ranging from 0 to $P_{N_1} \cdot \alpha_0$ (where α_0 is the degree of ionization for one element) are given to $P_{Me_1^+}$, it is possible to obtain a series of values for P_{N_2}/P_{N_1}, corresponding to different degrees of ionization α of the main element.

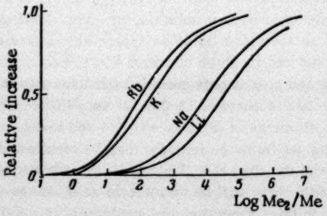

Fig. 3. The relation between the relative increase $(\alpha_0 - \alpha_1)/\alpha_0$ of cesium and the logarithm of the ratio of the concentration of the alkali metals added to cesium concentration. The cesium concentration in solution = 10^{-4} M; the maximum possible increase A = 22.3.

In order to calculate the increase which occurs on suppression of ionization, we calculate for each case the degree of ionization $\alpha_1 = P_{Me_1^+}/P_{N_1}$, and from this the relative increase $(\alpha_0 - \alpha_1)/\alpha_0$. The relative increase was calculated for cesium in this way for several cesium concentrations and one potassium concentration.

In Fig. 3 is shown one of a typical series of curves for cesium at a concentration of 10^{-4} M, using an acetylene flame (the theoretical maximum increase A=22.3). The curves for the relative increase have an S shape, while the upper and lower parts asymptotically approach the line of maximum increase and the abscissa. Curves for various metals are approximately parallel and are shifted in the middle along the abscissa by a value which corresponds approximately to the difference in the logarithms of the ionization constants of the corresponding metals. In other words, in order to evoke an equal relative increase, the concentrations of the metals added should be inversely proportional to their ionization constants. An appreciable relative increase (> 5%) for each of the added metals is observed starting at a certain concentration below which this metal has almost no effect on radiation intensity. Thus potassium starts to show an effect from concentrations which are twice that of cesium $[\log(P_{Me_2}/P_{Me_1})] = 0.3$, while sodium starts to show an effect at concentrations about 60 times that of cesium ($\log P_{Na}/P_{Cs} = 1.8$).

In Fig. 4 are shown curves for the relative increase in cesium under the influence of potassium and sodium for three cesium concentrations in solution (10^{-3}, 10^{-4}, and 10^{-5}M); log C (M) is plotted along the abscissa, not $\log(P_{Me_2}/P_{Me_1})$. An increase approximating to the maximum possible is not observed when the maximum concentration of the foreign metals of 1 M is used, either in the case of K or Na. Thus in the case of the latter element at $C_{Cs} = 10^{-4}$ and 10^{-5} M and $C_{Na} = 1$M, the increase is only half of the maximum possible. A conclusion of practical importance which can be drawn from this is that buffering with sodium salts does not lead to the desired results, and that the presence of additional amounts of potassium and rubidium salts in the solution will lead to an additional increase in the intensity of the cesium line. It is clear from Fig. 4 that at equal concentrations potassium or sodium affect the radiation intensity to the same extent when the cesium concentration is 10^{-4}-10^{-5}M; thus an equal increase in the relative intensity of the Cs line is obtained for different Cs concentrations. At $C_{Cs} = 10^{-3}$M, the effect of K and Na is weaker and a higher salt concentration is necessary to give the same relative increase. This fact is important for explaining the path taken by the curves relating the line intensity of the ionizing metal and its concentration in the presence of various constant concentrations of the other metal.

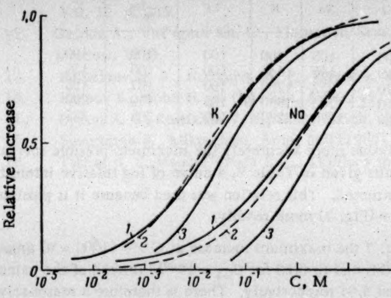

Fig. 4. The relation between the relative increase in cesium $(\alpha_0 - \alpha_1)/\alpha_0$ and the concentration of potassium and sodium salts in solution. 1) 10^{-5} M Cs; 2) 10^{-4} M Cs; 3) 10^{-3} M Cs.

Let us also consider the case of the effect of alkali metal salts on the radiation intensity of potassium. The potassium concentration chosen for calculation was 10^{-4}M, while the maximum increase = 4.2 for an acetylene flame. As is evident from Fig. 5, cesium at a concentration ratio Cs:K as low as 100-200 (i.e. at a cesium concentration of $1 - 2 \cdot 10^{-2}$M) leads to almost complete supression of ionization; under these conditions the relative increase amounts to 0.95. In the case of Na and Li, concentrations of 10-20 M ($\log P_{N_2}/P_{N_1} = 5.05$-$5.3$) are necessary to achieve the same end; at ordinary salt concentrations of the order of 1 M complete supression of ionization is not obtained.

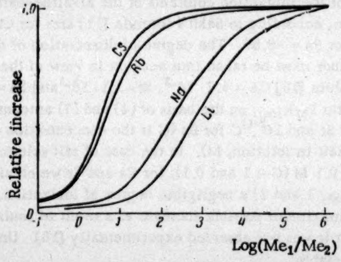

Fig. 5. The relation between the relative increase in potassium $(\alpha_0 - \alpha_1)/\alpha_0$ and the logarithm of the ratio of the concentration of the added alkali metals to potassium concentration ($C_K = 10^{-4}$M, A = 4.2).

Verification of the Calculations. In order to check on the conclusions derived from theory, experiments were carried out on the effect of K, Na, and Li on the radiation intensity of cesium in an acetylene flame. A comparison was made of the readings obtained for cesium radiation at 852.1 mμ on a flame spectrophotometer composed of a UM-2 monochromator, a photomultiplier, and a microammeter [5] when solutions of cesium salts (10^{-4} and 10^{-3}M) were sprayed directly into the flame, and the readings obtained when the same solutions to which Na, K, and Li salts had been added at concentrations of 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 1 M were sprayed into the flame. In order to eliminate the "anion effect" solutions of the nitrates of the alkali metals were used. The radiation intensity of Cs solutions to which no foreign salts had been added was taken as 100%. The results are given in Table 2.

The results are presented graphically in Fig. 6, a logarithmic scale being adopted for the concentrations of the alkali metals added.

The curves obtained have the shape of the initial branches of the S-shaped curves in Fig. 4.

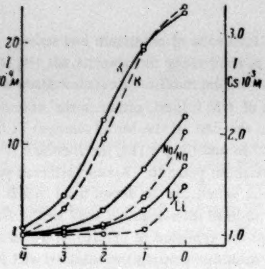

Fig. 6. The relation between the intensity of the cesium line and the logarithm of the concentration of added alkali metals. Continuous line: $C_{Cs} = 10^{-4}$M; dotted line: $C_K = 10^{-3}$M.

TABLE 2. Change in the Radiation Intensity of Cesium in an Acetylene Flame in the Presence of Other Alkali Metals

Concentration of alkali metal added, M	Relative intensity of the cesium line					
	at a Cs concentration of 0.0001 M in the presence of the metals			at a Cs concentration of 0.001 M in the presence of the metals		
	Li	Na	K	Li	Na	K
0,0001	103	105	150	100	100	100
0,001	119	145	444	100	105	125
0,01	170	352	1200	100	107	195
0,1	340	765	1980	105	140	290
1,0	780	1270	2260	150	205	325

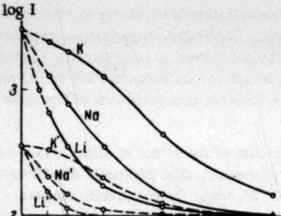

Fig. 7. The relation between the logarithm of the intensity of the cesium and $1/\sqrt[4]{C}$ (C is the concentration of added alkali metals). Continuous line: $C_{Cs} = 10^{-4}$M; dotted line: $C_{Cs} = 10^{-3}$M.

In order to determine more accurately the maximum possible increase on the basis of the results given in Table 2, a curve of log relative intensity against $1/\sqrt[4]{C}$ was constructed. This relation was used because it is possible to extrapolate to $C = \infty$ (Fig. 7) more readily.

According to Fig. 7 the maximum increase at $C = \infty$ ($1/\sqrt[4]{C} = 0$) amounts to 28.0 for $C_{Cs} = 10^{-4}$M, and to 3.63 for $C_{Cs} = 10^{-3}$M instead of the calculated values of 22.3 and 3.64 respectively. There is therefore a reasonably close agreement between the calculated values obtained on the basis of theory and the experimental results.

In conclusion it is interesting to consider the possible increase in the radiation of the alkaline-earth metals in a flame following upon ionization supression. The logarithms of the ionization constants of the alkaline-earth metals in an acetylene flame, according to Sakh's formula [11] are: for Ca = -10.45, for Sr = -9.55, and for Ba = -8.55. The degree of dissociation of the oxide (or hydroxide) compounds must be taken into account in view of their small values; we take the values [13] Ca = $4.7 \cdot 10^{-2}$, Sr = $1.1 \cdot 10^{-1}$ and Ba = $2.1 \cdot 10^{-3}$. From this, the ratio P_N/K_{ion}, on the basis of (4) and (7) amounts to $10^{5.42}$C for Ca, $10^{4.89}$C for Sr and $10^{2.17}$C for Ba (C is the concentration of the metal in the form of its salt in solution, M). In the case of salt solutions with concentrations of 1 and 0.1 M (C = 1 and 0.1), for Ca and Sr we obtain, on the basis of the curves (Figs. 1 and 2) a negligible degree of ionization, and an almost unobservable maximum possible increase as a result of ionization supression; in actual fact it was not observed experimentally [16]. Under these conditions, in the case of Ba, however, the value would be appreciable.

SUMMARY

The quantitative relations which hold during the increase in the radiation intensity of a metal in a flame as the result of ionization supression due to the presence of another metal have been considered. The degree of ionization of the metal atoms in the flame and the maximum possible increase following from complete conversion of ions into nonionized atoms depend on the ratio of the total partial pressure of atoms and ions in the flame to the ionization constant. The characteristic effects shown by other alkali metals on the radiation intensity of the test metal have been established. The theoretical deductions have been confirmed, taking as an example the increase in radiation intensity of cesium caused by the presence of other alkali metals in the flame of an acetylene-air mixture.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A FLUORESCENCE METHOD FOR DETERMINATION OF MICROAMOUNTS OF METALS IN THE FORM OF METAL-THIOCYANATE (HALIDE)–BASIC DYE COMPOUNDS

COMMUNICATION 1. DETECTION OF ZINC ON THE BASIS OF THE FLUORESCENCE EXTINCTION OF AQUEOUS SOLUTIONS OF RHODAMINE C

A. K. Babko and Z. I. Chalaya

T. G. Shevchenko State University, Kiev

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Rhodamine C (rhodamine B in the old nomenclature) is a valuable reagent for the photometric, extraction-photometric, and fluorescent determination of microamounts of gallium, thallium, indium, antimony, tungsten, etc. Methods for the detection and photometric determination of zinc with rhodamine C have been described [2-4]. On interaction with metals, sparingly soluble compounds $A_2[MeHal_4]$ are formed, in which A is the cation of the basic dye, Me is the metal, and Hal is halide or thiocyanate. It has been noted [4] that formation of the zinc thiocyanate rhodamine compound leads to extinction of the fluorescence of rhodamine C.

Our problem was to study the possibility of determining zinc in the form of a thiocyanate compound with rhodamine C by a fluorescent method. Our experiments confirmed published information [4] on the extinction of rhodamine C fluorescence. As the zinc concentration increases,the color of the fluorescence changes from orange to red. It should be possible therefore to develop a method for determining zinc on the basis of measurement of the fluorescence extinction of aqueous solutions of rhodamine C.

Fluorescence intensity was measured on an FM photometer of the Pulfrich type. A PRK-4 tube fitted with a UFS-3 filter 40 × 40 mm was used as the fluorescence excitation source.

Fluorescence extinction, like the change in color which is observed during formation of the zinc thiocyanate rhodamine compound, depends on a number of factors which have not been studied sufficiently. pH and thiocyanate concentration are the most important factors.

It was found that thiocyanate ions will lead to fluorescence extinction of rhodamine C in the absence of zinc, and also cause the color to change from orange to red, as well as causing a change in the color of rhodamine C from red-violet to blue. Published results on the interaction between thiocyanate ions and rhodamine C are contradictory, [1,2]. Accordingly, we carried out experiments under such conditions which ensured absence of zinc and other heavy metals present as impurities in the reagents and in the distilled water; the latter were purified beforehand with dithizone. These experiments confirmed published results [2] to the effect that thiocyante ions give a color reaction with rhodamine C, similar in its outward effect to the reaction of zinc thiocyanate ions.

In order to establish the optimum conditions for determining zinc, we next studied the relation between the formation of the two compounds,thiocyanate-rhodamine and zinc thiocyanate rhodamine, which can be formed in the zinc thiocyanate-rhodamine C system, and the pH and thiocyanate concentration.

These experiments showed that as the result of formation of zinc thiocyanate-rhodamine and thiocyanate-rhodamine the solutions become turbid; the fluorescence is, however, stable with time and there is no need to add a stabilizer. To get reproducible results and maximum fluorescence extinction of the rhodamine C, it is necessary to mix the solutions of zinc, thiocyanate, rhodamine C and water (to a definite volume). In all subsequent measurements, we kept to this order of adding the solutions.

The relation between the fluorescence of the system zinc thiocyanate rhodamine C and pH is shown in Fig. 1. A red filter was used for measuring the fluorescence; the reference solution was a solution of $1.6 \cdot 10^{-5}$M rhodamine C in a medium of 0.17 M potassium thiocyanate; the fluorescence of this solution was taken as 100%.

As Fig. 1 shows, at pH> 6 determination is in general impossible. This is connected with the state of the rhodamine (a pseudo base is formed), since under these conditions, in dilute solutions, neither the zinc thiocyanate ion nor the thiocyanate ions show any effect. At pH< 5.5 the presence of zinc leads to an extinction effect. This effect is strongly dependent on pH, and this is a drawback since during quantitative determination the pH has to be rigidly controlled. At pH<4.2 the main reagent—thiocyanate— gives the same effect, even in the absence of zinc (Curve 2). There is a short pH range with an optimum at 4.2-4.6 (Curve 4) for sensitive quantitative determination.

An analogous relation between change in rhodamine C color and pH was established spectrophotometrically (Fig. 2).

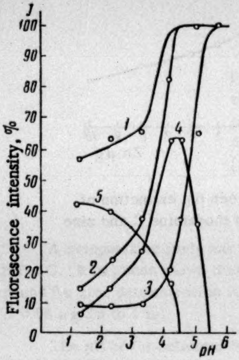

Fig. 1. Relation between fluorescence and pH in the system zinc thiocyanate-rhodamine C. 1) Fluorescence of rhodamine C; 2) ditto in the presence of thiocyanate; 3) ditto in the presence of thiocyanate and zinc; 4) the difference between the ordinates of curves 2 and 3; 5) difference between the ordinates of curves 1 and 2. $[Zn^{2+}]$ = [rhodamine] = 1.6×10^{-5}M; [KSCN]=0.17M.

Optical density was measured on a SF-4 spectrophotometer at λ = 590 mμ and l = 10 mm. The concentration of all the components was the same as during measurement of the fluorescence (see Fig. 2). A 0.5% freshly prepared solution of gelatin was added as stabilizer.

The relation between the fluorescence extinction of rhodamine C and thiocyanate concentration is shown in Fig. 3*. A red filter was used during fluorescence measurements, and the fluorescence standard was a 2×10^{-5}M solution of rhodamine C; the fluorescence of this solution was taken as 100%. The suitable thiocyanate concentration range was found to be 0.05-0.2 M with an optimum at 0.08-0.1 M (Curve 1). At [KSCN]< 0.05 M no extinction was observed, while at [KSCN] > 0.2 M, extinction was observed even in the absence of zinc.

The pH of 5 and the thiocyanate concentration [KSCN] of 0.17 M recommended in the literature are within the pH and thiocyanate concentration limits we established, although they are not the optimum values [3, 4].

In order to study the relation between the fluorescence extinction of aqueous rhodamine C solutions and zinc concentration, solutions were prepared by the method given for photometric determination of zinc [3]. The only difference was that the final volume we used was 6 ml (instead of 60 ml) while the amounts of all reagents were correspondingly decreased. The fluorescence intensity of solutions with varying zinc contents was measured using a red filter; the fluorescence standard was the solution in the blank test; its fluorescence was taken as 100%. The experimental results are given in Fig. 4.

As Fig. 4 shows, it is possible to determine zinc quantitatively by measuring the fluorescence extinction of an aqueous solution of rhodamine C. Over the zinc concentration range 1-4 μg Zn in 6 ml, the fluorescence extinction is linearly proportional to zinc concentration. When the zinc content increases from 4-10 μg the color of the fluorescence changes from orange to red, and differences in the fluorescence intensity of the solutions decrease. The reproducibility of the results is 2%. The sensitivity of a determination is 0.08 μg zinc in 1 ml.

The basic characteristics of the fluorescent and photometric methods [3] obtained on the basis of a series of zinc determinations are given in the table.

The absorption curves of the reagent and of the colored zinc compound, taken on an SF-4 spectrophotometer at l = 10 mm, are shown in Fig. 5.

It is clear from Fig. 5** that even when excess zinc is present the total (integral) light absorption changes by 5% in all; the second maximum is weakly expressed and the color change is not large enough. It is best to use a spectrophotometer, the optical density being measured at 590-600 mμ.

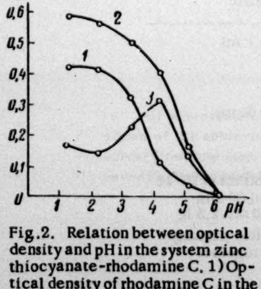

Fig. 2. Relation between optical density and pH in the system zinc thiocyanate-rhodamine C. 1) Optical density of rhodamine C in the presence of thiocyanate; 2) ditto in the presence of zinc; 3) the difference between ordinates of 2 and 3.

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*The thiocyanate concentration is plotted on a log scale.

**Results which have been published [3] were obtained during measurements on an FM photometer of the Pulfrich type using light filters, which essentially distort the actual relation of the absorption curves.

The decrease in fluorescence intensity of a solution, even in the presence of excess reagent (at a zinc content of 10 μg; see Fig. 4), amounts to 83%; this determines the high sensitivity of the fluorescent method of determination.

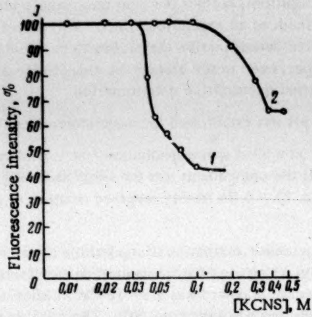

Fig. 3. Fluorescence of rhodamine C as a function of thiocyanate concentration. 1) In the presence of zinc; 2) without zinc. $[Zn^{2+}] = [\text{rhodamine}] = 2 \times 10^{-5}$M; pH 4.7.

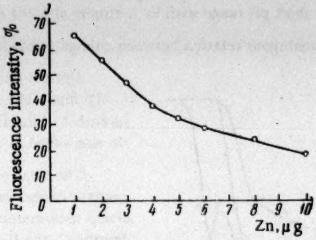

Fig. 4. Relation between the extinction of an aqueous solution of rhodamine C and zinc concentration.

The molar extinction coefficient calculated on the basis of published results on the composition of the zinc compound [2] and on the basis of our experimental results amounts to $6 \cdot 10^{-4}$ at λ_{590}. The disagreement between our results and published results ($E = 4.6 \cdot 10^{-4}$) is explained by the fact that we calculated the molar extinction coefficient for $\lambda_{max} = 590$ mμ (for the colored zinc compound), while the authors in [2] determined this value on an FÉK-M instrument fitted with a red filter, i. e., outside the region of maximum absorption of the colored zinc compound.

Basic Characteristics of the Fluorescent and Photometric Methods of Determining Zinc

Characteristics	Methods of determining zinc	
	Fluorescent	Photometric
Sensitivity	0.08 μg in 1 ml	0.13 μg in 1 ml
Relative experimental error	8-10%	15-25%
Concentration range over which determination is carried out	0.5-10 μg in 6 ml	8-25 μg in 60 ml
Final volume in the determination	6 ml	60 ml
Stability with time (optical density, fluoresence)	Does not change	For zinc contents of 25-15 μg in 60 ml, 30 min; 15 μg in 60 ml, 2.5 hr
Measurement time (of optical density, fluorescence)	Independent	One hour after pouring solutions together

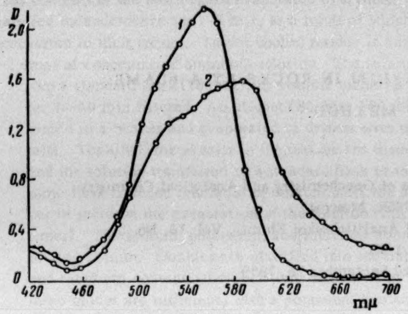

Fig. 5. Absorption curves of solutions of reagent and of the colored zinc compound. 1) Rhodamine C in the presence of thiocyanate. Rhodamine concentration = $5 \cdot 10^{-5}$ M; [KSCN] = 0.2 M; 2) Colored zinc compound. $[Zn^{2+}] = 3 \cdot 10^{-2}$ M.

SUMMARY

A comparative study has been made of photometric and fluorescent methods of determining zinc with rhodamine C. It has been shown that the most effective way of using formation of the zinc thiocyanate-rhodamine compound for zinc determination is to measure the fluorescence extinction of its solutions. The sensitivity of the method is 0.08 μg Zn in 1 ml.

The pH of the solutions is the most important factor which affects the color and the fluorescence. At pH > 6, rhodamine C forms a pseudo base which does not react with either zinc or thiocyanate; at pH < 4.2 thiocyanate ions form a colored and nonfluorescent compound similar to that formed by the zinc thiocyanate complex.

It has been established that the optimum pH and thiocyanate concentrations are about 4.2 and 0.1 M respectively.

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DETERMINATION OF CESIUM IN ROCKS BY A FLAME SPECTROPHOTOMETRIC METHOD

V. I. Lebedev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Isotope dilution [1,2] and neutron activation methods [3] are used for the determination of cesium in rocks and meteorites. These methods are fairly sensitive and completely reliable, but the requisite apparatus is expensive and not readily available—factors which limit their possibilities for solving geochemical problems. Consequently cesium is often determined by the comparatively less sensitive, but more readily available and readily carried out spectrographic methods. Fabrikova's published method [4] on flame photometric determination of hundredths and thousandths of a percent of cesium in minerals cannot be applied to the determination of 10^{-4}% Cs in rocks.

Determination of cesium at the hundreths and thousandths percent level can be carried out by a technique developed for rubidium [5,6] after chemical treatment. The method satisfies the requirements of geochemistry both from the point of view of sensitivity and accuracy.

Cesium was determined on an apparatus consisting of a monochromator and photomultiplier using an air-acetylene burner [5]. Potassium and rubidium strongly supress cesium emission. Nevertheless, at a relatively high potassium and rubidium content (at concentrations $K/Cs \geq 1500$-2000) the cesium emission is almost constant (Fig. 1). The ratio K/Cs in various rocks is usually somewhat greater than the ratio indicated, so that there is no need to add potassium to test samples in order to get the necessary sensitivity, as indicated already [4]. Large amounts of potassium and rubidium present in samples and standards create a high background which even at narrow monochromator slit widths is often considerably higher than the cesium emission. The accuracy with which the background is measured in such cases is strongly reflected in the accuracy with which cesium is determined, this being particularly true when a monochromator with low dispersion is used.*

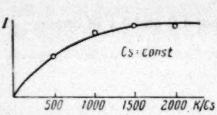

Fig. 1. Effect of potassium on cesium emission.

It is known that the background, which is determined by the lines of the elements which are located close to the test line, falls off exponentially, not linearly, and that in the case of a line with high intensity it leads to a certain error if the mean arithmetic value of the background is calculated from measurements made on both sides of the analytical line. In order to calculate the background more accurately we adopted the technique of measuring the background at three points for a standard solution not containing cesium; on this basis we calculated the value of the background in the test solution from the relationships $I^0_{b_1}/I^0_{b\lambda} = I^x_{b_1}/I^x_{b\lambda}$ and $I^x_{b_2}/I^0_{b\lambda} = I^x_{b_2}/I^x_{b\lambda}$ (where b = background) and not from their sum (see Fig. 2).** The method cannot be used when the intensity of cesium emission is considerably less than the background intensity when a monochromator of low dispersion is used. Preliminary chemical treatment is readily carried out [7].

Analytical Procedure. A one-g aliquot of finely ground silicate rock is moistened in a platinum baisn with distilled water; 20-25 ml of hydrofluoric acid and 1 ml of sulfuric acid are added and the mixture carefully heated on a hot-plate until white fumes appear. The contents of the basin are stirred from time to time with a platinum spatula. When necessary, some more hydrofluoric acid is added. After evaporation to remove fluorides completely, a few drops of water are added and the contents of the basin again evaporated to dryness. The dry residue is calcined in the basin over a gas burner to a pale red incandescence for 1-2 min, as a result of which iron, aluminum, and some of the magnesium and calcium are converted to their oxides. To the cooled residue is added 50-70 ml of water, 0.5 g of ammonium carbonate, and 1-2 drops of concentrated ammonia solution. The mixture is transferred without filtration into a standard flask (100 ml), its volume made up to the mark, and after standing for 30-40 min filtered. An aliquot (80 from 100 ml of 160-170 ml from 200) is collected in a beaker and evaporated to dryness with nitric acid to remove ammonium salts. The alkali metal salts in the residue are dissolved in a small volume of water and the solution transferred to a standard flask or to a calibrated test tube. To this same flask is added methanol or ethanol until the alcohol concentration is 40% in order to increase the evaporation of the solution (this increases the sensitivity 2-2.5 times). The sodium, potassium, and rubidium contents are established before determining cesium. Samples are classified into several groups with differing potassium and rubidium contents (the potassium content is of basic importance); usually two or three groups are sufficient, with a potassium content of less than 1% in group I, 1-4% in group II, and 4-10% in group III. Standard solutions with approximately the same sodium, potassium, rubidium, and alcohol contents are prepared corresponding to each of these groups. The standard solutions contained the following amounts of cesium: 0.0; 0.1; 0.2; 0.5; 1.0; 1.5; 2.0; 3.0 μg/ml. Photometric measurements are made on the basis of the 852 mμ Cs line.

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*We also used an ISP-51 spectrograph provided with an outlet slit for determination of cesium in rocks. Here the background value decreased strongly; the mean value of the background was calculated as the mean arithmetic value of the background on both sides of the line.

**A recording of part of the spectrum taken from Poluektov's book is reproduced in Fig. 2 [9].

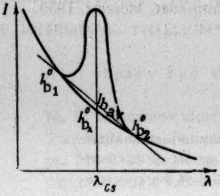

Fig. 2. Calculation of background value during cesium determination.

TABLE 1

Amount of Cs^{137} added cpm	Value of aliquot %	Activity of the aliquot, cpm	Cesium separated, %
1280	80	997	78
1280	85	1023	80
1280	87.5	1080	84.5

The completeness of separation of cesium by the method indicated was checked by adding known amounts of cesium 137 to a sample before decomposition. As the results in Table 1 show, the loss error does not exceed 5%.

The accuracy and reproducibility of the method was checked on synthetic solutions prepared from pure potassium, rubidium, and cesium salts (Table 2), and also by repeated cesium determinations on standard G-1 and several other samples (Table 3).

TABLE 2

Taken μg/ml			Cs found μg/ml	Error, %
Cs	Rb	K		
0,12	10,0	980	0,11	−8,3
0,48	15,0	1960	0,50	+4,0
0,96	15,0	1960	0,99	+3,0
1,44	20,0	1960	1,39	−3,1
0,24	10,0	980	0,26	+8,3

TABLE 3

Sample	Found n · 10^{-4}%				Mean value	Published results [8]
G-1	2,2 2,1	2,0 1,9	1,8	2,1	$2,0 \cdot 10^{-4}$	$2,2 \cdot 10^{-4}$
Syenite No. 143	3,1 3,1	2,8	3,2	2,8	$3,0 \cdot 10^{-4}$	

The method has been used for determination of cesium in silicate rocks and also for the determination of 1×10^{-4} % to 7×10^{-4}% of rubidium in stone meteorites.

SUMMARY

A method is described for the determination of cesium in rocks; elements of the second and third groups are removed by chemical concentration. When instruments with low resolving power are used, it is recommended that the flame background be measured at three points using a solution free from cesium.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

COMMUNICATION 6. NEW COMPLEXOMETRIC METHODS OF DETERMINING THALLIUM*

A. I. Busev and V. G. Tiptsova

M. V. Lomonosov Moscow State University

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Original article submitted January 29, 1959

The instability constant of the complex of trivalent thallium with sodium ethylenediaminetetraacetate (EDTA-Na) at 20° and at an ionic strength of 0.1 is $10^{-22.5\pm0.5}$ [1]. Accordingly it should be possible to carry out direct complexometric titration of Tl^{3+} at pH 2 using 1-(2-pyridylazo)-2-naphthol as indicator [2], and at pH 4-5 using xylenol orange [3]. Titration of Tl^{3+} at pH 2 possesses high selectivity; Cd, Zn, and Pb do not interfere. Fe^{3+}, Bi, Cu, Ni, and In interfere, as well as Cl^-, Br^-, and I^-; the latter three form complexes with Tl^{3+} at pH 2-3 which are more stable than those formed with the indicator**. Indirect methods which have been used are based on titrating excess EDTA-Na with standard solutions of Co^{2+} (indicator – SCN^-) [4], Th^{IV} (indicator–alizarin S) [5], Zn^{2+} (indicator–ferri-ferrocyanide mixture and benzidine) [6], V^V (indicator–diphenylcarbazide or diphenylcarbazone) [7], or on potentiometric titration with a Zn^{2+} salt using a Hg electrode as indicator [8]. In all the indirect methods described, titration was carried out at pH 3.5-5.0; this leads to a drop in selectivity.

For Tl^{3+} determination we have adopted the technique of titrating excess EDTA-Na with a standard solution of ferric alum in the presence of sulfosalicylic acid at pH 2; this technique permits determination of Tl^{3+} in the presence of Cd^{2+}, Zn^{2+}, Pb^{2+} and ≤0.1 M Cl^-. This is a decisive advantage of the method compared with direct titration at pH 2. Br^- ions interfere at pH 2.

For determination of trivalent thallium, 2 N NH_4OH solution is added to the test solution until a turbidity of $Tl(OH)_3$ appears; the latter is dissolved by addition of a few drops of concentrated HCl; 10 ml of standard EDTA solution is added, followed by five drops of 20% sulfosalicylic acid solution; the liquid is heated to 40-60° and titrated with a standard solution of $Fe(NH_4)(SO_4)_2$ until the yellow-green color of iron EDTA changes to an orange-red color (the result of the superposition of the red-brown color of iron sulfosalicylate on the yellow-green color) which does not disappear in the course of of one minute. Results are given in Table 1. Bi, In, Fe, and Cu interfere.

Separate determination of trivalent iron and thallium is based on the following. Trivalent thallium ions at pH 3 form a more stable complex with Br^- ions than with EDTA-Na. Br^- ions accordingly permit Tl^{3+} to be masked at pH 2. Under these conditions Fe^{3+} reacts with EDTA-Na quantitatively. After titration of Fe^{3+} ions at pH 2 in the presence of Br^- using sulfosalicylic acid as indicator, the pH of the solution is adjusted to 4-5 and trivalent thallium titrated using 1-(2-pyridylazo)-2-naphthol (or pyridylazoresorcinol) as indicated.

To the solution containing Fe^{3+} and Tl^{3+} is added 5-10 ml of 2 M KBr; NH_4OH is then added until the pH is 2; the liquid is heated to 40-60° and trivalent iron titrated with EDTA-Na solution until the red-brown color disappears. By adding CH_3COONH_4 the pH is adjusted to 4-5; a few drops of 0.1% pyridylazoresorcinol are added until a distinct red color*** shows; the trivalent thallium is then titrated with EDTA-Na solution until the color of the solution changes to orange-yellow. A distinct color change is only observed when the iron content is not too high. At Fe^{3+} concentrations not exceeding that of Tl^{3+}, both titrations can be carried out with the same EDTA-Na solution: at higher Fe^{3+} concentrations the EDTA-Na solution used for the first titration should be more concentrated. The method for separate complexometric titration of trivalent iron and thallium gives satisfactory results (Table 2).

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*Communication 5, see Zh. analit. khimii 15, 573 (1960).

**Halide ions do not interfere at pH 4-5, but the selectivity of the method with respect to the cations decreases sharply.

*** So that the rose color of the complex of Tl^{3+} with the indicator shows up more clearly against the yellow colored background arising from the iron EDTA complex, excess of the indicator must be added; accordingly, taking into account the limited solubility of 1-(2-pyridylazo)-2-naphthol in water, it is best to use water-soluble pyridylazoresorcinol.

TABLE 1. Indirect Determination of Trivalent Thallium

Tl taken, mg	0.01169 M $Fe(NH_4)(SO_4)_2$ used, ml	Tl found, mg	Error, mg	Tl taken, mg	0.01169 M $Fe(NH_4)(SO_4)_2$ used, ml	Tl found, mg	Error, mg
12,61	3,28	12,52	—0,09	3,78	6,88	3,92	+0,14
12,61	3,25	12,60	—0,01	3,78	6,95	3,75	—0,03
12,61	3,22	12,66	+0,05	2,52	7,48	2,48	—0,04
6,30	5,95	6,14	—0,16	2,52	7,45	2,55	+0,03
6,30	5,90	6,26	—0,04				

TABLE 2. Separate Determination of Trivalent Iron and Thallium in Each Others Presence

Taken, mg		EDTA-Na solution used, ml		Found, mg		Taken, mg		EDTA-Na solution used, ml		Found, mg	
Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl
1,31	6,30	2,35*	3,00	1,31	6,11	20,40	6,30	3,20**	3,10	20,33	6,30
2,61	6,30	4,70*	3,05	2,62	6,21	20,40	6,30	3,25**	3,15	20,55	6,41
3,92	6,30	6,99*	3,15	3,89	6,41	40,80	6,30	6,45**	3,18	40,80	6,47
3,27	5,67	5,86*	2,84	3,36	5,78	40,80	3,15	6,48**	1,50	40,98	3,06

* EDTA-Na solution 0,009965 M, same for Fe and Tl.

** EDTA-Na solution 0.1132 M.

TABLE 3. Separate Determination of Trivalent Bismuth and Thallium in Each Others Presence

Taken, mg		Solution used, ml		Found, mg		Taken, mg		Solution used, ml		Found, mg	
Bi	Tl	0.1132 M EDTA-Na	0,01052 M $Cu(NO_3)_2$	Bi	Tl	Bi	Tl	0.1132 M EDTA-Na	0,01052 M $Cu(NO_3)_2$	Bi	Tl
39,0	6,30	1,98	2,98	38,8	6,40	39,0	12,61	2,13	5,85	37,6	12,58
78,0	6,30	3,58	2,95	78,3	6,34	97,5	6,30	4,35	2,90	96,5	6,23
19,5	6,30	1,10	2,95	19,6	6,34	97,5	2,52	4,15	1 10	95,5	2,36
19,5	12.61	1,35	5,90	19,2	12,69						

Successive determination of Cu^{2+} and Tl^{3+} is not feasible, since at pH 2, Tl^{3+} is titrated together with Cu^{2+} in the presence of Br^-; this is related to the smaller difference in the stabilities of their complexonates under these conditions. Successive titration of Bi^{3+} and Tl^{3+} is also impossible since BiOBr is precipitated in the presence of Br^- at pH 1.5-2. The following technique has been used for the separate determination of trivalent bismuth and thallium. Total Bi^{3+} and Tl^{3+} are titrated at pH 4-5 in the presence of 1-(2-pyridylazo)-2-naphthol or pyridylazoresorcinol; Tl^{3+} is then reduced to Tl^+ by means of Na_2SO_3 and the EDTA-Na thereby liberated titrated with standard $Cu(NO_3)_2$ solution.

To the test solution containing Bi^{3+} and Tl^{3+} is added dry ammonium acetate until the pH is 4-5 (the solution should remain clear), then a few drops of 0.1% methanol solution of 1-(2-pyridylazo)-2-naphthol, and the resultant solution is titrated with EDTA-Na solution until the indicator color changes to yellow; about 0.1 g Na_2SO_3 is added, followed by some more indicator and the solution titrated with $Cu(NO_3)_2$ solution until the color of the solution changes from yellow to red-violet. Satisfactory results were obtained in this way, particularly for high amounts of thallium

The end point during direct complexometric titration of trivalent thallium can be established by making use of the interaction of the iodide complexes of trivalent thallium with EDTA-Na. As our experiments showed, the iodide complexes of trivalent thallium are so stable that at pH <6 they do not react with EDTA-Na, while at pH 6-8 this reaction proceeds quantitatively. Starch can be used as indicator (taking into account the specific characteristics of the iodide complexes of trivalent thallium) [9]: while trivalent thallium not bound as the complexonate is present in solution, i.e., TlI_4^- ions exist in the presence of I^-, then I_3^- ions will also be present at which color the starch blue; the blue color disappears at the end point.

To the test solution (3-30 mg Tl in 80-100 ml) is added several ml of 1 M tartaric acid; NH_4OH is then added until the color of the tropeoline 000 added changes from yellow-orange to rose; 1 M tartaric acid solution is next added until the yellow-orange color appears, and 1 ml of 1% KI is added (a yellow color, not rose, should appear at this stage; the rose color appears when the amount of KI added is not sufficient for formation of I_3^-; in such a case it is necessary to add a little more KI, a large excess being avoided because of the possibility of liberation of TlI). The final solution is titrated with EDTA-Na until the color changes from intense yellow to pale yellow; a few ml of 1% starch solution is added and titration continued until the blue color disappears. The method gives satisfactory results and possesses satisfactory reproducibility (Table 4).

TABLE 4. Complexometric Determination of Trivalent Thallium in the Presence of Starch-Iodide Indicator

Thallium, mg		Error		pH on completion of titration	Thallium, mg		Error		pH on completion of titration
taken	found	mg	%		taken	found	mg	%	
3,15	3,15	0	0	7,6	12,61	12,61	0	0	7,3
3,15	3,26	+0,11	+3,5	7,6	12,61	12,01	—0,60	—5	8,2
5,04	5,39	+0,35	+7	5,2	25,22	25,35	+0,13	+0,5	7,5
5,04	5,25	+0,21	+4	5,7	25,22	25,22	0	0	7,5
5,04	5,09	+0,05	+1	7,3	31,52	31,67	+0,15	+0,5	7,8
12,61	12,73	+0,12	+0,9	7,6					

At pH >8 low results are obtained, while at pH <6 high results are obtained. The method is not selective and many elements interfere.

SUMMARY

A method has been developed for the indirect complexometric determination of thallium at pH 2. The possibility has been demonstrated of carrying out successive complexometric titration of trivalent iron and thallium, and of bismuth and thallium. It has been established that the iodide complexes of trivalent thallium react stoichiometrically with EDTA-Na at pH 6-8, so that it has been possible to develop a complexometric method for determining thallium with a starch-iodide indicator.

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QUANTITATIVE DETERMINATION OF SCANDIUM BY MEANS OF HALOGEN-SUBSTITUTED MANDELIC ACID

I. P. Alimarin and Shen Han-Si

M. V. Lomonosov Moscow State University

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In a previous communication [1] we suggested a new method for determining scandium by means of mandelic acid; the scandium mandelate precipitate, however, has a comparatively high solubility in water. It was of considerable interest therefore to study halogen substituted mandelic acid as a precipitant for scandium. The introduction of electrophilic groups into an aromatic nucleus is known to lead to an increase in the sensitivity of precipitation; the introduction of halogens into the benzene ring increases the acid properties of the reagent and leads to a decrease in the solubility of the compounds formed with metals, and also to a decrease in the solubility of the reagent itself in water. It has been found that p-halogenomandelic acids quantitatively precipitate scandium from moderately acid solution, and that the solubility of the compound decreases with increasing molecular weight of the reagents.

EXPERIMENTAL

Reagents Used. Para-chloro-, p-bromo-, and p-iodomandelic acids were studied in the course of the work described here as precipitants for scandium. Apart from bromomandelic acid, we synthesized the reagents by Klingenberg's method [2]. By recrystallization from benzene it is possible to obtain pure preparations with m.p. 118-119° for p-iodomandelic acid. The values which we found for the solubility of the reagents in water at 20° are given in Table 1.

Study of Precipitation of Scandium with p-Halogenomandelic Acids. In order to establish the optimum conditions for precipitating scandium we studied the effect of the amount of the reagents and of the pH of the solution by a method described earlier [1]. It was found that considerably less of the p-halogenomandelic acids is required for complete precipitation of scandium than is the case when mandelic acid is used. Usually a concentration of 0.02 M p-chloro- or p-bromomandelic acid, and not more than 0.01 M p-iodomandelic acid, is enough to ensure precipitation.

TABLE 1. Solubility of Mandelic Acid and Its Halogenated Derivatives in Water at 20°

Acid	Solubility in water	
	moles per liter	g/liter
Mandelic Acid*	1.0	160.0
p-Fluoromandelic acid*	0.57	97.0
p-Chloromandelic acid	0.12	20.4
p-Bromomandelic acid	0.11	25.4
p-Iodomandelic acid	0.022	6.2

*The results on the solubility of mandelic acid and p-fluoromandelic acid determined by Belcher et al. have been included for comparison [3].

It is clear from Fig. 1 that scandium is precipitated in the acid range by p-chloro- and p-bromomandelic acids in the same way as by mandelic acid. Complete precipitation of scandium iodomandelate occurs at pH about 1 and higher; in the alkaline range, however, the interaction products of scandium with the given acids strongly differ from scandium mandelate.

Scandium mandelate is readily soluble in ammonia, forming $[NH_4]_3[Sc(C_8H_6O_3)_3]$, so that at pH > 3.2 scandium is not precipitated completely. The compounds of scandium with p-chloro- and p-bromomandelic acid are also soluble in alkaline media, but more sparingly soluble than scandium mandelate. The chloromandelate starts to dissolve at pH 4.0, while the bromomandelate starts to dissolve at pH 5. Moreover, on boiling these alkali solutions, rapid hydrolysis of the compound is observed with partial precipitation of the hydroxide or basic salts of scandium. Scandium iodomandelate, which does not form a similarily soluble complex compound, hydrolyzes when subjected to the effect of ammonia, and all the precipitate is converted into scandium hydroxide. It follows from these observations that the introduction of a halogen into the benzene ring of mandelic acid leads to a decrease in the stability of the complex compounds of scandium in an alkaline medium.

Next we determined the composition of the compounds isolated from acid media and washed with ether and ethanol. Scandium was determined by calcining the compound dried at 110° to the oxide, while the organic part was determined by cerimetric titration according to a method described by Verma [4,5]. The water of crystallization content was determined by difference and was also confirmed thermogravimetrically. The composition of the compounds (Table 2) is in good agreement with the formula $H_3[Sc(Hal \cdot C_8H_5O_3)_3] \cdot H_2O$, where Hal = Cl, Br, I.

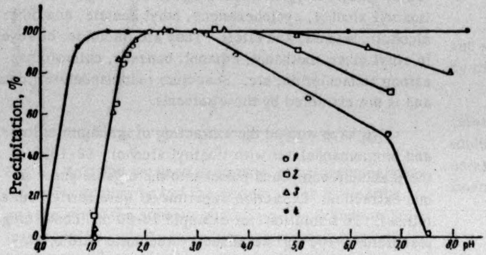

Fig. 1. Completeness of precipitation of scandium by mandelic acid and its halogeno derivatives as a function of the pH of the solutions. -o-o- scandium mandelate; -□-□- scandium chloromandelate; -Δ- scandium bromomandelate; -●-●- scandium iodomandelate.

Thermogravigrams of scandium halogenomandelates (Fig. 2) show that crystallization water contained in the compounds is removed at 120-160°. Decomposition of the compound starts at 260-280°, while over the range 500 to 540° the compounds are converted to scandium oxide.

For determination of the solubility of the series of compounds of scandium with mandelic acid and its halogeno derivatives, the precipitates obtained were washed with ether and ethanol, dried at 110°, placed in flasks and then shaken for about 40 hr at 20° until equilibrium was reached. The precipitates were filtered off at the end of this period and scandium determined photometrically in a known volume of the filtrates. Results for the solubility of scandium mandelate and halogenomandelates in water are given in Table 3.

TABLE 2. Results of Analyses of the Compounds

Compound	Sc, %		$Hal \cdot C_8H_6O_3$, %		H_2O, %	
	calculated	found	calculated	found	calculated	found
$H_3[Sc(Cl \cdot C_8H_5O_3)_3] \cdot H_2O$	7,47	7,42	89,63	89,92	2,90	2,66
$H_3[Sc(Br \cdot C_8H_5O_3)] \cdot H_2O$	5,97	6,04	91,63	91,85	2,40	2,11
$H_3[Sc(I \cdot C_8H_5O_3)_3] . H_2O$	5,03	4,87	92,86	93,26	2,01	1,87

Determination of Scandium in Solutions of Its Salts and in the Presence of the Rare Earths. Results for determination of scandium by means of p-halogenomandelic acids are given in Table 4. The methods permit determination of milligram amounts of scandium in 100 ml of solution.

TABLE 3. Solubility of Scandium Mandelate and Halogenomandelates in Water at 20°

Compound	Solubility in water	
	moles per liter	g/liter
Scandium mandelate	$8.8 \cdot 10^{-5}$	0.03986
Scandium chloromandelate	$1.6 \cdot 10^{-5}$	0.00896
Scandium bromomandelate	$1.3 \cdot 10^{-5}$	0.00904
Scandium iodomandelate	$6.5 \cdot 10^{-6}$	0.00537

The rare earths are precipitated by these acids at high pH values. For example, the chloro- and bromomandelates of the rare earth elements of the cerium group are precipitated at pH values higher than 3.5, while the iodomandelates of these elements are precipitated at pH about 2.5. These reagents therefore permit separation of scandium from the rare earths.

As an example we have studied in detail the possibility of determining scandium in the presence of cerium group rare earths by means of p-bromomandelic acid. Experiments showed that the rare earths are partially coprecipitated with scandium when only one precipitation is carried out; reprecipitation is therefore necessary.

Thorium should be absent since it is also precipitated by the reagents under indentical conditions; thorium can however be complexed with citric acid. Table 5 contains results for the separation of scandium from cerium group rare earths.

Extraction of the Compounds with Organic Solvents. Scandium mandelate is insoluble in common solvents, and it only floats in some of them. The introduction of halogens into the benzene ring of mandelic acid, particularly introduction of chlorine and bromine, leads, however, to an increase in the extractability of the complex compounds. Scandium chloro- and bromomandelates are readily extracted by several oxygen-containing solvents, e.g., n-butanol, isoamyl alcohol, cyclohexanone, ethyl acetate, and other alcohols, ketones, and esters. They are insoluble, however, in ethyl ether, methanol, ethanol, benzene, chloroform, carbon tetrachloride, etc. Scandium iodomandelate floats and is not extracted by these solvents.

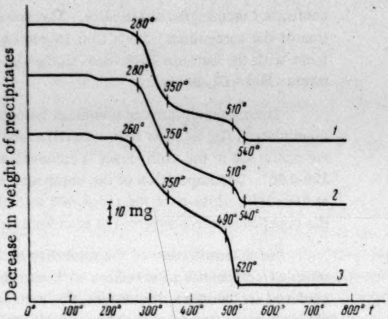

Fig. 2. Thermogravigrams. 1) Scandium chloromandelate; 2) scandium bromomandelate; 3) scandium iodomandelate.

We have studied the extraction of scandium chloro- and bromomandelates with isoamyl alcohol. 98-100% of the scandium compound passes into the organic phase in one extraction. Extraction experiments were carried out as follows. To a solution (for example 10-20 ml) containing scandium (5-100 μg) we added hydrochloric acid or ammonia to control the pH. Scandium was then extracted with a 0.01 M solution of p-chloro- or p-bromomandelic acid in isoamyl alcohol, the volume of which was the same as that of the aqueous phase. After the phases had separated out, scandium was determined photometrically in both the aqueous and organic phases. The scandium in the organic phase was reextracted with 1 N hydrochloric acid. Fig. 3 shows the relation between the extraction of the chloro- and bromomandelates of scandium and the cerium group rare earths and the pH of the solution; it follows from Fig. 3 that by using an extraction method it is possible to extract microamounts of scandium, and to separate it from large amounts of the rare earths. Table 6 contains results on the separation of scandium from cerium-group rare earths by extraction of the bromomandelates with isoamyl alcohol at pH 3.0-3.5.

TABLE 4. Determination of Scandium in a Solution of Its Salt by means of p-Halogenomandelic Acids

Reagent	Sc_2O_3, mg		Error, %
	taken	found	
Cl—C_6H_4CH(OH)·COOH	0,98	1,00	+0,02
	4,93	4,94	+0,01
	9,86	9,85	—0,01
Br--C_6H_4—CH(OH)·COOH	1,01	1,02	+0,01
	3,03	3,03	±0,00
	10,10	10,10	±0,00
I —C_6H_4—CH(OH)—COOH	0,98	0,96	—0,02
	4,93	4,95	+0,02
	9,86	9,88	+0,02

TABLE 5. Determination of Scandium in the Presence of Cerium Group Rare Earths by Means of p-Bromomandelic Acid

Sc_2O_3, mg		Ratio Sc_2O_3 : :(total rare earths)$_2O_3$	No. of precipitations	Error, mg	Sc_2O_3, mg		Ratio Sc_2O_3 : :(total rare earths)$_2O_3$	No. of precipitations	Error, mg
taken	found				taken	found			
3,03	3,98	1 : 1	1	+0,95	2,02	2,10	1 : 10	2	+0,08
3,03	3,00	1 : 1	2	—0,03	3,03	2,99	1 : 10	2	—0,04
10,10	10,02	1 : 1	2	—0,08	1,01	1,08	1 : 50	2	+0,07
10,10	10,15	1 : 1	2	+0,05	1,01	0,96	1 : 100	2	—0,05

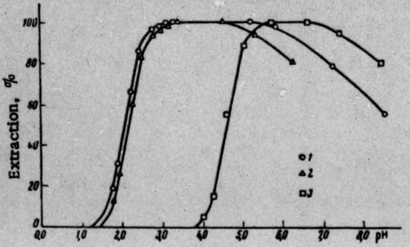

Fig. 3. Relation between extraction of halogenomandelates of scandium and of the cerium group rare earths and the pH of the aqueous phase. -o-o- Scandium bromomandelate; -Δ-Δ- scandium chloromandelate; -□-□- bromomandelates of cerium group rare earths.

SUMMARY

Precipitation of scandium with p-halogenomandelic acids has been studied. The composition of the precipitates formed corresponds to the formula $H_3[Sc(Hal \cdot C_8H_5O_3)_3] \cdot H_2O$ (where Hal = Cl, Br, I).

Methods have been developed for the determination and separation of scandium from cerium-group rare earths by means of p-halogenomandelic acids.

Extraction of scandium p-bromo- and p-chloromandelates with water-immiscible organic solvents has been studied, and it has been shown that scandium can be separated from cerium group rare earths by extraction with isoamyl alcohol.

TABLE 6. Separation of Scandium from Cerium Group Rare Earths by Extraction

Sc_2O_3, µg		Ratio Sc_2O_3 : : (total rare earths)$_2O_3$	Error, µg	Sc_2O_3, µg		Ratio Sc_2O_3 : : (total rare earths)$_2O_3$	Error, µg
taken	found			taken	found		
25,0	24,8	1 : 50	—0,2	10,0	10,0	1 : 2500	±0,0
25,0	24,5	1 : 50	—0,5	10,0	9,6	1 : 2500	—0,4
25,0	24,3	1 : 250	—0,7	10,0	9,6	1 : 5000	—0,4
25,0	25,3	1 : 250	+0,3	10,0	10,1	1 : 5000	+0,1
15,0	14,5	1 : 500	—0,5	5,0	5,1	1 : 5000	+0,1
15,0	15,0	1 : 500	±0,0	5,0	4,9	1 : 5000	—0,1
15,0	14,6	1 : 1000	—0,4	5,0	5,7	1 : 10 000	+0,7
15,0	14,8	1 : 1000	—0,2	5,0	5,8	1 : 10 000	+0,8

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SPECTROGRAPHIC DETERMINATION OF GERMANIUM AND OTHER ELEMENTS IN ORES WITH SULFIDATION OF THE LATTER DURING THEIR EVAPORATION*

A. K. Rusanov, V. M. Alekseeva, and N. V. Il'yasova

All-Union Scientific Research Institute of Mineral Raw Material, Moscow

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Increasing the Sensitivity of the Determination of Elements during Sulfidation of Samples. The fractional evaporation effect is used very widely during spectrographic determination of small amounts of elements in ores, minerals, and other objects. When the rate of fractional distillation of compounds of the test elements is high enough, the concentration of their atoms in the cloud of the light source increases significantly, the intensity of the lines of the elements increases with respect to the background of the spectrum, and consequently the sensitivity of their determination increases.

The use of fractional evaporation of elements for increasing the sensitivity of their determination is only possible in some cases by effecting corresponding changes in the chemical composition of the test materials. This can be realized during the evaporation process in the spectrum excitation source by adding appropriate reagents to the test material [1-5]. The basic condition which decides the choice of reagent is that formation of readily volatile compound of the impurity elements should proceed sufficiently rapidly, while the elements present in large amounts in the test material should form compounds which are sparingly volatile compared with compounds of the impurity elements.

Our observations show that an appreciable increase in the sensitivity of determination is observed in many cases for elements which form readily volatile sulfides, on adding sulfur powder to test oxide and other ores, and evaporating the mixture of powders in a reducing medium from the electrode crater of a carbon arc used for spectrum excitation. Under such conditions, one would expect the greatest increase in sensitivity for those elements whose sulfide compounds differ sharply from their oxide compounds in their vaporizability.

In Fig. 1 is shown a comparison of the duration of evaporation of equal atomic amounts of elements when they are introduced into the crater of a carbon electrode in the form of their sulfides or oxides, in the absence of compounds of other elements. 1×10^{-4} g-atom of the respective elements was evaporated from the crater of a carbon electrode 3.5 mm in diameter and 5 mm deep. The arc was fed with an ac current of 8 amp, 220 v. The amount by weight of the evaporated compounds was varied in accordance with their molecular weight; the weights used varied from 5 to 25 mg.

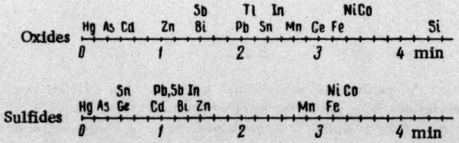

Fig. 1. Duration of evaporation of 1×10^{-4} g-atom of the elements in the form of their sulfides and oxides from the crater of an ac carbon electrode arc.

As Fig. 1 shows, on switching from the oxides to the corresponding sulfides a very significant increase in the rate of evaporation is observed in the case of germanium; the evaporation rate of lead sulfide and particularly of tin sulfide also exceeds the evaporation rate of their oxides. No large differences are observed in the rate of evaporation of oxide and sulfide compounds of the remaining elements.

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* Reported at the All-Union Conference on the Analysis of Rare and Semiconducting Elements, convened by GEOKhI, AN SSSR (Moscow, December 1959) and at the Conference on Spectrographic Analysis of Ores for Rare and Scattered Elements convened by the Ministry of Geology and Conservation of Mineral Resources of the USSR (Tashkent, April 1959).

It should be noted that on switching from oxides to sulfides the change in evaporation conditions shown in Fig. 1 is only maintained in those cases where the elements are present in the test ore in the form of oxides, distributed as isolated mechanical impurities which react rapidly in a reducing medium with sulfur, and do not react with the main element of the sample to form new, sparingly volatile compounds. A significant increase in the sensitivity of determination is achieved on evaporating, in the presence of sulfur, quartz and silicate powders containing the oxide compounds of microelements which tend to form sulfides, the oxides being present as mechanical impurities.

In those cases where the elements to be determined are present in the form of isomorphous impurities, or, after fusion of the test sample, enter into the composition of the melts formed, the chemical composition of the melts affects their capacity to evaporate. In this connection therefore there may be a divergence from the changes in evaporation rate of the elements on going from oxides to sulfides shown in Fig. 1. Accordingly, in choosing reagents which modify the composition of the test sample during its evaporation, one must be guided not only by the capacity of the impurity elements to form readily volatile compounds in an isolated state, but also by the capacity of the melts of the freshly formed materials to retain the impurity elements.

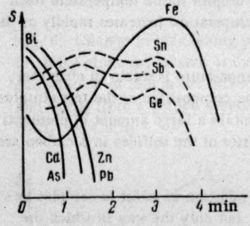

Fig. 2. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide from a carbon electrode crater.

The effect of the composition of the melts on the evaporation rate of the elements is shown most often in those cases where the oxides are analyzed; consequently, sulfidation of oxide ores, whose melts in many cases retain the test elements fairly strongly, has undoubted practical importance. Thus during evaporation of iron oxide ores, the melts of the latter strongly retain germanium, tin, and antimony, and separate passage of these elements and iron into the arc cloud is impossible. The lines of germanium, tin, and antimony are observed together with those of iron in the spectrum of the arc cloud throughout evaporation of an iron ore from the electrode crater (Fig. 2).

The picture of the change in intensity of the lines of germanium, antimony, and tin is totally different when a mixture of iron oxides and sulfur in the proportion 2:1 is evaporated. Under these conditions germanium, tin, and antimony evaporate completely in 50-90 sec in the arc cloud from the melt of iron sulfides formed rapidly in the electrode crater.

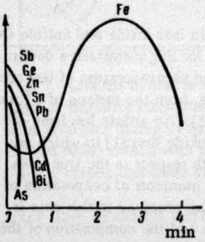

Fig. 3. Change in the blackening of lines of impurity elements present as oxides on evaporating a mixture of iron oxide and sulfur from a carbon electrode crater.

Under such conditions the iron mainly passes into the arc cloud only after complete evaporation of germanium, tin, and antimony; thus the rion background which is characteristic of the spectrum is absent on the spectrogram. A comparison of Figs. 2 and 3 shows that on adding sulfur to iron oxide ores, the time taken by lead, cadmium, zinc, and bismuth to pass into the arc cloud is also shortened; these elements evaporate during the initial burning stages of the arc. An examination of Figs. 4 and 5 indicates that addition of sulfur to quartz containing the oxides of impurity elements leads to rapid evaporation of chalcophilic elements in the arc flame.

In the absence of sulfur, part of the impurity elements present as oxides succeed in combining with the quartz before evaporation to form silicates, and when the melts are not heated strongly enough are firmly retained by the latter.

It should be borne in mind that the evaporation conditions indicated in Figs. 2-5 relate to the case where the arc is fed by an ac current, force-ignited by high-frequency currents; there is a spot in the arc at which there is less heating of the electrodes than in a dc arc or in the case of a free burning ac arc. Thus during evaporation of ores in a dc arc from the crater of a carbon anode the passage time of the elements is shortened, and it is possible to evaporate from silicate melts into the arc flame not only Hg, As, Pb, Cd, Bi, and Zn, but also Ge, Sn, and Sb if the arc is allowed to burn long enough.

In most cases, addition of sulfur to test ores containing large amounts of iron, quartz, and silicates leads to a significant increase in the sensitivity of the determination of elements which form volatile sulfides. Evaporation of about 20 mg of iron oxide ores in the presence of sulfur from the electrodes leads to an increase in the sensitivity of determination from 1×10^{-3} - 7×10^{-4} to 1×10^{-4}% in the case of germanium.

Increase in sensitivity depends to a large extent on the amount of sample placed in the electrode, since this amount determines the amount of microelements passing from the sample into the arc cloud. Accordingly, the highest sensitivity is achieved on evaporating the test samples from chamber electrodes heated independently, up to 10 g of test material being used [3, 6-9].

On evaporating 0.4 g of an iron oxide ore mixed with sulfur from chamber electrodes independently heated, it is possible to detect 1×10^{-5} - 7×10^{-6}% of germanium on the basis of its 2651.2 A line. Under these conditions it is also possible to determine 1×10^{-5}% cadmium, thallium, tin, antimony, bismuth, arsenic, and zinc in iron oxide ores.

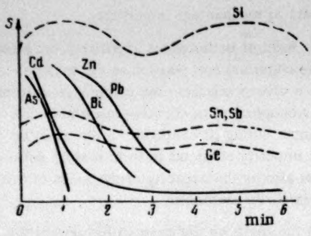

Fig. 4. Change in blackening of lines of impurity elements present as oxides on evaporating quartz from a carbon electrode crater.

On adding sulfur to the test sample a vigorous evaporation of sulfur in the arc flame occurs. The ionization potential of sulfur (10.4 ev) is lower than the effective ionization potential established in an arc cloud burning between spectrographically pure carbon electrodes; the appearance of sulfur, despite the fact that its ionization potential is high enough, leads during the initial stages of burning to a drop in flame temperature from 7400 to 4600°K. Subsequently the arc temperature increases rapidly as the sulfur evaporates.

The indicated change in flame temperature is stable in character, and only depends to a small extent on the composition of the test samples in those cases where the latter do not contain a large amount of elements which occur early on in the volatility series of the sulfides in a carbon arc [10].

It should also be pointed out that addition of sulfur to samples being evaporated determines to a large extent not only the way in which the flame temperature changes, but also the conditions for diffusion removal of the impurity elements from the arc cloud. Accordingly, addition of sulfur favors an increase in the reproducibility of the determination of trace elements passing simultaneously with sulfur into the arc cloud. Addition of sulfur also prevents sputtering of the sample, sputtering being frequently observed, e.g., during evaporation of iron oxide ores.

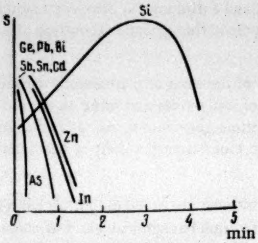

Fig. 5. Change in blackening of lines of elements present as oxides on evaporating quartz mixed with sulfur from a carbon electrode crater.

Quantitative Determination of Germanium in Iron Oxide and Sulfide Ores, Silicates, and Coal Ash. Most published methods for the quantitative determination of 1×10^{-2} - 4×10^{-4}% germanium are based on evaporation of test ores and coal ash from the crater of a carbon electrode, from the surface of a rotating metallic electrode or from paper strips [12-21]. An article has been devoted to the determination of germanium in iron oxide ores [1] in which use is made of the increase in the germanium line with respect to the iron lines and to the spectrum background during the initial moments of evaporation of the ore. The incomplete evaporation of germanium observed in this case is determined by the relationship between the results and the composition of the test ore.

During the search for germanium in iron oxide ores a method which attracted attention was one which permitted determination of 4×10^{-4}% germanium; germanium determination was based on blowing the powdered ore into the cloud of a horizontally arranged ac arc [22]; using this blowing technique, incomplete evaporation of the germanium from the ore was again observed.

As noted earlier, conditions for complete and rapid evaporation of germanium are attained on sulfidation of iron oxide ores during their evaporation from the crater of a carbon electrode.

Additions to iron oxide ores of reagents ($SnCl_2$, $CuCl_2$) which are capable in a reducing medium of forming volatile germanium chlorides, and also addition of crystalline iodine, which gives volatile germanium iodides, as is evident from Figs. 6 and 7, do not give better results than those obtained when the germanium is evaporated from iron oxide ores by addition of sulfur. The characteristic way in which germanium passes into the arc cloud during evaporation of a mixture of an ore with iodine is determined by the fact that a considerable amount of germanium does not succeed in reacting with iodine, since the latter volatilizes very rapidly from the electrode crater.

Neither does germanium distill into the arc cloud with the requisite rapidity and completeness on adding various salts of the alkalimetals (KCl, KI, KIO_3 etc.) or on addition of potassium pyro-antimonate; these salts lower the temperature of the arc and the melt and favor distillation with them of the volatile compounds of the elements from the melt.

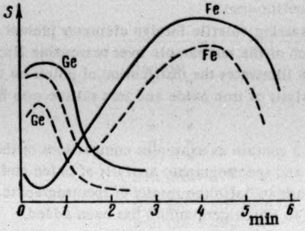

Fig. 6. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide mixed with $SnCl_2$ and $CuCl_2$ from a carbon electrode crater. $SnCl_2$ —; $CuCl_2$ - - - .

Analytical Procedure. The test powder of iron oxide ore is mixed in the proportion of 2:1 with powder consisting of equal parts by weight of sulfur and quartz, and the whole ground in an agate mortar in the presence of alcohol. 0.5% of antimony oxide, which is used as an internal standard, is added beforehand to the powder, which is mixed with test ore. Sixty mg of the mixture of ore, sulfur, and quartz powder is introduced into the opening in a spectrographically pure carbon electrode. The diameter of the opening is 3.5 mm while its depth is 5 mm, and the wall thickness is 1 mm. This electrode is fixed at a distance of 3 mm below the upper electrode, which is a spectrographically pure carbon electrode sharpened to a cone. The electrodes are fixed by means of their shadow projections in a position which will ensure that during the first moments after the arc has been ignited the image obtained of the central part of the arc flame will fall on the diaphragm of the intermediate lens. The slit is illuminated by means of a three-lens illuminating system. The spectra are photographed with an ISP-28 quartz spectrograph "Spectrographic" Type 2 plates, with a sensitivity of 16 GOST units. The arc is fed with a current of 8 amp at 220v from a DG-2 ac arc generator.

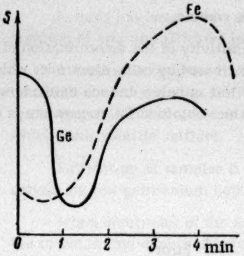

Fig. 7. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide mixed with iodine from a carbon electrode crater.

The spectra are photographed in the course of the first 100 sec after the arc has been ignited; this time is sufficient for all the germanium to evaporate from the test sample.

Calibration curves constructed within the coordinates ΔS vs $\log C$ are used for calculating the germanium concentration of test samples. When the germanium concentrations in the samples are low (0.0001-0.0002%) the curves are constructed within the coordinates $\log(I/I_{\text{int. standard}})$ vs $\log C$; the background intensity is subtracted from the line intensities.

Standard ore samples whose germanium contents have been established fairly accurately by chemical analysis are used for constructing the calibration curves. When no ore samples are available whose germanium contents have been established chemically, ore powders free from germanium can be taken and known weights of germanium dioxide added to them. Standard powders are prepared by successive dilution, 2-3 times, of a standard powder with a high germanium content with ore free from germanium. The dilution process should be accompanied each time be careful mixing and grinding of the powders in an agate mortar.

TABLE 1

Analytical lines	Concentration ranges over which germanium was determined, %	Lines of interfering elements	Control lines of interfering elements	Approximate concentration of interfering elements, %
Ge I 2651.18 and Sb 2670.64	0.0001−0.01	Pb bands 2647−2659		>10
		Zn 2670.53	Zn 2682.8	> 5
Ge I 2651.18 and Sb I 2877.92	0.0001−0.01	Pb bands 2647−2659		>10
		Cr 2877.98	Cr 2875.99	>1

Table 1 contains the wave lengths of the analytical pairs of lines, the germanium concentration ranges determined, and the lines of elements which interfere with germanium determination.

Experience has shown that the technique suggested can be used for analyzing not only iron oxide ores but also iron sulfide ores, silicates, and coal ash.

When ores are converted into sulfides, the effect of comparatively sparing volatile foreign elements present in large amounts in the test sample decreases, and changes in the composition of the test sample over reasonable limits do not lead to the appearance of systematic errors. As an example, Fig. 8 illustrates the distribution of points on the curve constructed within the coordinates ΔS, log C for the case of the analysis of iron oxide and iron sulfide ores from different ore deposits, and for coal ash.

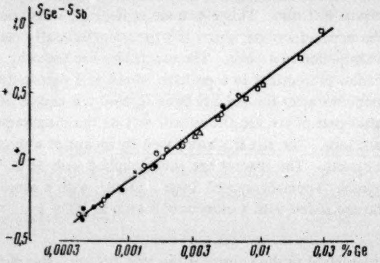

Fig. 8. Relation between difference in blackening of the lines Ge I 2651.18 and Sb 2670.64 and germanium concentration of a test sample. ● Iron oxide ore; o magnetic fraction; × martite ore; Δ polmetallic ore; □ coal ash.

Tables 2 and 3 contain as examples comparisons of the results of chemical and spectrographic analysis of oxide and sulfide ores and coal ash and also the results of spectrographic analysis of ore samples to which germanium has been added.

The probable error of a duplicate determination of germanium proved to be 6%. The error may increase 1.5-2 times in the case of the lowest germanium contents.

The technique indicated has been used over a long period for the analysis of iron oxide ores containing germanium. One spectroscopist in the course of a working day can analyze 15 ore samples for their germanium content.

As noted above the sensitivity of the determination of germanium in ores can be increased by using electrodes which can hold a larger amount of test sample. In such cases, however, the reproducibility in the values obtained for germanium is observed to fall off.

TABLE 2.

Composition of sample	Ge, %		Ge, % mean	Error (relative), %
	spectrographically	chemically		
Iron ore	0,0052	0,0049	0,0050	+4
" "	0,00067	0,00066	0,000665	+3
" "	0,00085	0,0010	0,0009	−5,5
" "	0,0014	0,0017	0,0015	−6,5
Magnetic fraction	0,0020	0,0018	0,0019	+10
" "	0,0046	0,0050	0,0048	−4
" "	0,0068	0,0065	0,0066	+3
" "	0,0014	0,0012	0,0013	+4
" "	0,0006	0,0006	0,0006	±0
" "	0,00040	0,00045	0,00042	−4,5
Martite ore	0,00046	0,00050	0,00048	−4
" "	0,0012	0,0010	0,0011	+10
Hematite ore plus quartz	0,00040	0,00045	0,00042	−4,5
	0,00040	0,00045	0,00042	−4,5
Polymetallic ore	0,0032	0,0033	0,00325	−1,5
	0,0028	0,0035	0,0031	−10
Coal ash	0,030	0,026	0,028	+ 7
" "	0,009	0,010	0,0095	+5
" "	0,023	0,025	0,024	− 4
" "	0,0044	0,0045	0,00445	−10
" "	0,0070	0,0077	0,0073	− 4

TABLE 3

Composition of sample	Ge, %		Error (relative) %
	taken	found	
Iron ore	0,00028	0,00029	+3,6
" "	0,00028	0,00027	−3,6
" "	0,00028	0,00035	+25
" "	0,00055	0,00057	+3,6
" "	0,00055	0,00059	+7,3
" "	0,00055	0,00046	−16,3
" "	0,00055	0,00065	+18,2
Iron ore + 50% Al_2O_3	0,0013	0,0013	±0
Iron ore + 50% MnO_2	0,0013	0,0013	±0
Iron ore + 50% MgO	0,0013	0,0014	+8
Iron ore + 50% CaO	0,0013	0,0015	+16
Iron ore + 50% TiO_2	0,0013	0,0013	± 0
Iron ore + 50% SiO_2	0,0013	0,0011	−16
Iron ore + 50% of a mixture consisting of equal amounts of Al_2O_3, MnO_2, MgO, CaO, TiO_2, SiO_2	0,0013	0,0013	± 0

SUMMARY

A study has been made of the conditions under which chalcophilic elements pass into the arc cloud during evaporation of ores and silicates in the presence of sulfur.

A method is suggested for the analysis of oxide ores, coal ash, silicates, and other materials in which the test materials are subjected to sulfidation during their evaporation from the crater of a carbon electrode; this technique opens up possibilities of increasing the sensitivity, reproducibility, and accuracy of the determination of elements which form volatile sulfides.

Sulfidation of samples is particularly effective in the analysis of iron oxide ores, in which it is very difficult to determine low germanium contents.

When electrodes of the usual type containing 60 mg of a mixture of test sample and sulfur are used, it is possible to determine quantitatively 0.0002% of germanium in ores, silicates, and coal ash with an error of ±6%; use of chamber electrodes capable of holding larger samples leads to a 10- to 20-fold increase in sensitivity.

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2-(4-CHLORO-2-PHOSPHOBENZENEAZO)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID (CHLORPHOSPHONAZO I) AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF SEXIVALENT URANIUM

A. A. Nemodruk, Yu. P. Novikov, A. M. Lukin, and I. D. Kalinina

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, and the All-Union Scientific Research Institute
of Chemical Reagents, Moscow

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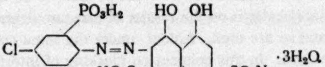
Reagents containing the arsono group [1-7] have found wide application for the photometric determination of uranium. Among these, azo derivatives of chromotropic acid with the arsono group in the position ortho to the azo group have proved particularly effective for this purpose; this is especially true of 2-(2-arsonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid, often called uranon or arsenazo [8,9].

Since phosphoric acid, which is similar in many respects to arsenic acid, forms more stable compounds with sexi- and quadrivalent uranium than does arsenic acid, it might be expected that the corresponding organic derivatives of phosphoric acid should also form more stable compounds with uranium. In this connection a study of the corresponding organic derivatives of phosphoric acid is of interest and worth carrying out.

The absence of published results on the use of colored organic reagents containing the atomic group PO_3H_2 for the photometric determination of a series of metals, including uranium, is a consequence of the fact that no methods are known for preparing the corresponding compounds. Several of these compounds are being synthesized at present by Lukin et al.[10]. The present article contains results of a study of 2-(4-chloro-2-phosphobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (which we have designated chlorphosphonazo I for short) as a reagent for the photometric determination of sexivalent uranium. The composition and structure of chlorphosphonazo I correspond to the formula:



Chlorphosphonazo I is very soluble in water; neutral and acid solutions have a red color, while alkaline solutions are violet. Weakly acid solutions of chlorphosphonazo have a maximum light absorption at 515 mμ (see Fig. 1, Curve 1). The position of the absorption maximum is independent of pH over the range 4.0-7.5 (see Fig. 2, Curve 1). On adding a number of metals to weakly acid solutions of chlorphosphonazo I the color of the solutions change from red to violet; in the case of sexivalent uranium to blue. Chlorphosphonazo I behaves in the same way as arsenazo, which also only forms a blue color with sexivalent uranium. The light absorption maximum of solutions of the compound of chlorphosphonazo I with sexivalent uranium occurs at 605 mμ (see Fig. 1, Curve 2); the molar extinction coefficient is 23,100; The molar extinction coefficient of the corresponding compound of sexivalent uranium with arsenazo is 22,800 [6], or 22,900 according to other results [4]. Thus the sensitivity with which uranium can be determined with chlorphosphonazo I is approximately the same as that when arsenazo is used.

A study of the relation between the light absorption of solutions of the compound of chlorphosphonazo I with sexivalent uranium and pH showed that the shape of the light absorption curves and the height of the maximum (Fig. 2 curve 2) hardly change at all over the range pH 5.2-8.0. The light absorption of solutions of the compound of uranium with chlorphosphonazo I, in contrast to that of solutions of the corresponding compound with arsenazo, is independent of the pH of the solutions over fairly wide limits; the value of the light absorption of the corresponding solutions of the compound of sexivalent uranium with arsenazo is different for almost all pH values [4]. As a result of this, during determination of uranium by means of chlorphosphonazo I, small variations in acidity cannot lead to changes in light absorption, and for this reason do not affect the accuracy of uranium determination.

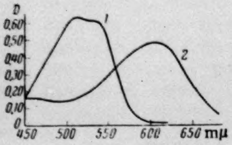


Fig. 1. Light absorption of solutions of chlorphosphonazo I and of its compound with sexivalent uranium as a function of wave length (SF-4 spectrophotometer; cuvette with layer thickness of 1 cm; optical density measured relative to water). 1) 2×10^{-5}M solution of chlorphosphonazo I, pH 6; 2) chlorphosphonazo I, 2×10^{-5}M and $UO_2(NO_3)_2$ 3×10^{-5}M, pH 6.

Chlorphosphonazo, in contrast to arsenazo, permits determinations to be carried out in more acid solutions. This is another advantage, since on carrying out determinations at lower pH values, it is possible to diminish or completely avoid interference from a number of masking agents (tartrates, citrates, oxalates, ethylenediaminetetracetic acid).

Chlorphosphonazo interacts with sexivalent uranium in the molar proportion of 1:1 (Fig. 3). Similar results were obtained both by the isomolar series method, and by the method of varying the concentration of one of the components while that of the other component is kept constant. The sharp break on the curves indicates that the compound formed has a fairly high stability. On the basis of the results obtained, the instability constant, calculated on the basis of the isomolar series method [11] was found to be 4×10^{-5}; this is greater than the corresponding value for the arsenazo compound, which is 5×10^{-3} [6].

In order to establish the extent of interference from other elements present on the determination of sexivalent uranium by means of chlorphosphonazo I, the amount of a particular element which would lead to an error of 5% in the determination of uranium was determined. For this purpose, 1.5×10^{-6} mole of uranyl nitrate (3.57 ml of a solution containing 0.100 mg uranium/ml) was introduced into each of five 100-ml standard flasks; to the first four flasks were then added various amounts of a solution of the element whose interference it was required to study, and the volume of the liquid in each flask was made up to 85-90 ml. Next, 2-ml lots of an acetate buffer with pH 5.5 were added and 3.0-ml lots of 0.001 M chlorphosphonazo solution; the volumes of the solutions in each flask were made up to the mark with water and the optical density measured on a SF-4 spectrophotometer at 605 mm in a cuvette with a layer thickness of 1 cm The value of the optical density of the solution free from the interfering element was taken as 100%. A curve of optical density (%) against content of interfering element was then constructed. From this curve the amount of interfering element which would increase or decrease the optical density by 5% was determined (Table 1).

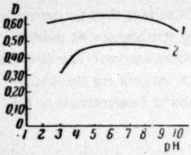


Fig. 2. The relation between light absorption of solutions of chlorphosphonazo I and of its compound with sexivalent uranium and pH (SF-4 spectrophotometer, cuvette with layer thickness 1 cm; optical density was measured relative to water). 1) 2×10^{-5}solution of chlorphosphonazo I at $\lambda_{max} = 515$ mμ; 2) solution of the compound at $\lambda_{max} = 605$ mμ (chlorphosphonazo I concentration 2×10^{-5}M; concentration of $UO_2(NO_3)_2$ 3×10^{-5} M.

The alkali and alkaline earth elements, as well as ions such as chloride, nitrate, sulfate, perchlorate, and acetate, do not interfere with uranium determination.

As the results in Table 1 show, there is no essential difference in the interference from metal cations on the results of uranium determination whether chlorphosphonazo I or arsenazo are used. Anions under the same conditions interfere to a considerably lesser extent. In this connection masking of interfering elements during determination of uranium with chlorphosphonazo I is more effective than is the case when arsenazo is used.

Since interference from a number of elements is fairly high during determination of uranium in solutions which have a complex composition, it is necessary to carry out a preliminary separation of uranium by extraction with tributyl phosphate or other extractants.

Method. To 1-5 ml of test solution is added 25 ml of a 60% ammonium nitrate solution containing 0.25% sodium ethylenediaminetetracetate (EDTA-Na); dilute ammonia solution (1:1) is next added until the pH is 2.5-3.0 (until the violet color of methanyl yellow changes to a rosy yellow) and the uranium extracted with 15 ml of a 20% solution of tributyl phosphate in carbon tetrachloride; the organic phase is filtered through a dry filter into another funnel. The aqueous layer is extracted once again with 10 ml of the 20% solution of tributyl phosphate in carbon tetrachloride. The combined extracts are washed with 25 ml of 60% ammonium nitrate solution, and after removal of the aqueous phase, the uranium is reextracted from the organic phase with 15 ml of a 0.005% solution of chlorphosphonazo I in a buffer mixture with pH 5.2 (25 g of sodium acetate and 5 ml of glacial acetic acid in 1 liter of solu-

TABLE 1. The Interfering Effect of Elements on the Photometric Determination of Uranium with Chlorphosphonazo and Arsenazo

Interfering elements of ions	The form in which the element or ion was taken	Proportion by weight of interfering element or ion to amount of uranium, which leads to an error of 5% in uranium determination	
		chlorphosphonazo	arsenazo
Al	$Al(NO_3)_3 \cdot 9H_2O$	1 : 70(+)*	1 : 70(+)
Be	$Be(NO_3)_2 \cdot 3H_2O$	1 : 70(+)	1 : 70(+)
Sn^{IV}	$SnCl_4$	1 : 35(—)	1 : 30(—)
Zr	$Zr(NO_3)_4 \cdot 5H_2O$	1 : 20(+)	1 : 25(+)
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	1 : 20(—)	—
Fe^{III}	$Fe(NO_3)_3 \cdot 9H_2O$	1 : 15(+)	1 : 15(+)
Th	$Th(NO_3)_4 \cdot 4H_2O$	1 : 12(+)	1 : 15(+)
Bi	$Bi(NO_3)_3 \cdot 5H_2O$	1 : 12(—)	—
Tc^{III}	$Tl(NO_3)_3$	1 : 12(—)	—
Tc^{I}	Tl_2SO_4	1 : 7,5(—)	—
Ce^{IV}	$Ce(OH)(NO_3)_3 \cdot 3H_2O$	1 : 5(+)	—
Rare earths	Nitrates	1 : 3,5(+)	—
Hg^{II}	$Hg(NO_3)_2 \cdot 0{,}5\ H_2O$	1 : 3,5(—)	—
V^{IV}	$(VO)SO_4$	1 : 3,5(—)	—
Co	$Co(NO_3)_2$	2 : 1(—)	—
Mn^{II}	$Mn(NO_3)_2$	3,0 : 1(+)	—
Cr^{III}	$Cr(NO_3)_3 \cdot 9H_2O$	3,0 : 1(+)	—
Ni	$Ni(NO_3)_2$	10 : 1(—)	—
Cd	$Cd(NO_3)_2$	30 : 1(+)	—
Zn	$Zn(NO_3)_2$	70 : 1(—)	—
$C_4H_5O_7^{3-}$	Ammonium citrate	3,5 : 1(—)	1 : 1
$C_4H_4O_6^{2-}$	Potassium tartrate	15 : 1(—)	4 : 1
$C_2O_4^{2-}$	Potassium oxalate	1 : 1(—)	1 : 4
EDTA-Na		6 : 1(—)	2 : 1
F^-	NH_4F	2 : 1(—)	1 : 4
VO_3^-	NH_4VO_3	10 : 1(—)	2 : 1
PO_4^{3-}	Na_2HPO_4	15 : 1(—)	3 : 1
$Cr_2O_7^{2}$	$K_2Cr_2O_7$	70 : 1(—)	10 : 1

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*The + sign denotes a positive error, while — denotes a negative error.

TABLE 2. Photometric Determination of Sexivalent Uranium with Chlorphosphonazo

U^{VI} taken, μg	Optical density of the aqueous phase	U^{VI} found, μg	Error, %	U^{VI} taken, μg	Optical density of the aqueous phase	U^{VI} found, μg	Error, %
5	0,034	5,00	0	75	0,507	74,55	—0,6
10	0,069	10,15	+1,5	100	0,685	100,7	+0,7
15	0,103	15,15	+1,0	125	0,845	124,2	—0,6
30	0,203	29,85	—0,5	150	1,010	148,5	—1,0
50	0,337	49,56	—0,9				

tion). After removal of the organic phase, the optical density of the colored aqueous phase is measured on an SF-4 spectrophotometer at 605 mμ in a cuvette with a layer thickness of 1 cm, relative to a 0.005% chlorphosphonazo solution. The uranium content is found by means of a calibration curve (Fig. 4); the calibration curve is constructed on the basis of a standard solution of uranyl nitrate containing 25 μg uranium/ml. The experimental error does not exceed ±1.5% (Table 2).

Zirconium, thorium, iron, beryllium, and aluminum present in the original test solution in amounts respectively 150, 450, 500, 1500, and 5000 times greater than the amount of uranium do not interfere with the determination. Interference from other elements is considerably less.

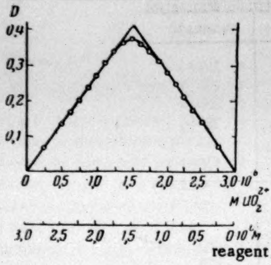

Fig. 3. Molar ratios during interaction of chlorphosphonazo I with UO_2^{2+}.

Synthesis of Chlorphosphonazo.* To 2.07 g (0.01 mole) of 5-chloro-2-aminobenzenephosphonic acid (for preparation of this compound see [10]) are added 30 ml of water and 2 ml of concentrated hydrochloric acid; a solution of 0.85 g sodium nitrite in 5 ml of water is added dropwise at 0-7°. The solution of 5-chloro-2-diazobenzenephosphonic acid obtained is added to 5.0 g (0.1 mole) of chromotropic acid dissolved in 75 ml of 10% sodium acetate solution. After the reaction mixture has been stirred for 10-15 min it is acidified with hydrochloric acid (sp.gr. 1.18) until an acid reaction to Congo red is obtained. The product which separates out is filtered off and then redissolved on heating in 50 ml of water; after this solution has cooled the material is reprecipitated by addition of 25 ml of hydrochloric acid. The precipitate is filtered off, washed with 5% hydrochloric acid solution, and dried at 90-100°; the yield is 2.6 g. When the product is heated further to constant weight at 160°, it loses 8.78% by weight; this corresponds to three molecules of water of crystallization

Found %: P 5.62; S 11.48; N 5.09; Na 4.05

$C_{16}H_{11}O_{11}N_2S_2PClNa$. Calculated %: P 5.35; S 11.41; N 4.99; Na 4.11

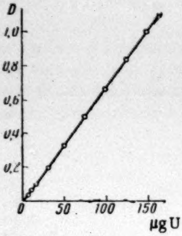

Fig. 4. Calibration curve for the determination of sexivalent uranium with chlorphosphonazo I (spectrophotometer SF-4, cuvette with layer thickness 1 cm, wave length 605 mμ; the optical density was measured with respect to a 0.005% chlorphosphonazo I solution).

SUMMARY

It has been shown that 2-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (called chlorphosphonazo I for short) is suitable for the photometric detremination of sexivalent uranium, and possesses properties similar to those of 2-(2-arsenobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (arsenazo). The main difference between chlorphosphonazo I and arsenazo is that the compound which chlorphosphonazo I forms with sexivalent uranium is more stable than the corresponding compound formed between uranium and arsenazo, so that uranium can be determined in solutions with higher acidity when chlorphosphonazo I is used. When sexivalent uranium is determined by means of chlorphosphonazo I, interference from masking agents is also considerably less.

A photometric method for the determination of sexivalent uranium with chlorphosphonazo I is suggested, in which uranium is separated beforehand from interfering elements by extraction.

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* G. B. Zavarikhina participated in this part of the work.

ISOLATION OF URANIUM AS AMMONIUM URANYL PHOSPHATE AND ITS GRAVIMETRIC DETERMINATION BY CALCINATION TO $U_2O_3P_2O_7$

A. E. Klygin, D. M. Zavrazhnova, and N. A. Nikol'skaya

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Of the series of sparingly soluble compounds formed during the interaction of uranyl ions with phosphoric acid, ammonium uranyl phosphate $NH_4UO_2PO_4 \cdot 3H_2O$ is the most valuable in analytical practice. Unfortunately, the solubility product of this compound ($4.36 \cdot 10^{-27}$ at 19-20°) has only been determined by dissolving the solid phase in solutions of nitric and sulfuric acids [1]. Published results on the possibility of a gravimetric determination of uranium by calcination of this compound to uranyl pyrophosphate are contradictory [2,3], and the calcination process itself requires some special precautions [2]. We decided therefore to determine the solubility product of $NH_4UO_2PO_4 \cdot 3H_2O$, and to establish the possibility of determining uranium gravimetrically by calcining this compound to $U_2O_3P_2O_7$.

The ammonium uranyl phosphate used for the present studies was prepared as follows: 100 g of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ and 40 g of ammonium nitrate were dissolved in 500 ml of 2 N nitric acid. The solution obtained was heated to 80° and 26 g of diammonium hydrogen phosphate, dissolved in a small volume of water, added. A bright-yellow precipitate immediately appeared. After cooling to room temperature, the precipitate was filtered off and washed six times with distilled water. Uranium was determined in the air-dried product by the hydrosulfite-phosphate method [4]; ammonium was determined acidimetrically after distilling it off as ammonia; phosphorus was determined colorimetrically with vanadate-molybdate [5], and water by Karl Fischer reagent. The salt obtained was found to contain 62.16% UO_2^{2+}, 3.93% NH_4^+, 21.36% PO_4^{3-}, and 12.46% H_2O, i.e., it has the composition $NH_4UO_2PO_4 \cdot 3H_2O$.

A thermogravigram obtained by E. P. Cherstvenkova for this salt is shown in the figure. Interpretation of the pyrolysis curve shows that the following processes occur on heating:

Conversion temperature, range, °C	Process	Loss in wt., %	
		found	calculated
20—120	$NH_4UO_2PO_4 \cdot 3H_2O \rightarrow NH_4UO_2PO_4 + 3H_2O\uparrow$	12,42—12,46	12.36
275—350	$NH_4UO_2PO_4 \rightarrow UO_2HPO_4 + NH_3\uparrow$	4,46— 4,85	4,45
500—700	$2UO_2HPO_4 \rightarrow (UO_2)_2P_2O_7 + H_2O\uparrow$	2,55— 2,52	2,32
700—1100	$2(UO_2)_2P_2O_7 \rightarrow 2(U_2O_3)P_2O_7 + O_2\uparrow$	2,30— 2,19	2,24

In order to confirm the correctness of the results obtained during pyrolysis of ammonium uranyl phosphate, and to choose the gravimetric form in which uranium is to be determined, the following experiments were carried out:

a) on drying $NH_4UO_2PO_4 \cdot 3H_2O$ in a vacuum desiccator the salt gradually gives up its water of crystallization;

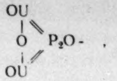
b) at 120-220° anhydrous ammonium uranyl phosphate is obtained, which absorbs water from the atmosphere;

c) on calcining the preparation at 400°, uranyl hydrophosphate UO_2HPO_4 is obtained, which is also hygroscopic;

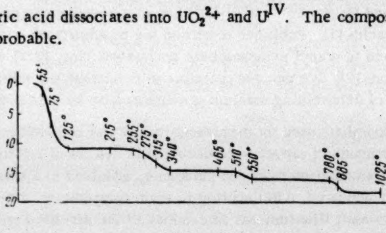
d) uranyl pyrophosphate $(UO_2)_2P_2O_7$ exists over a narrow temperature range; accordingly, it is only by strict control of temperature and calcining time that it is possible to get a compound with the composition indicated above;

e) the compound with composition $U_2O_3P_2O_7$ is readily obtained by calcining ammonium uranyl phosphate, uranyl hydrophosphate, and uranyl pyrophosphate at 900°. On increasing the temperature further its composition does not change (checked up to 1200°). The compound $U_2O_3P_2O_7$ has a yellow-green color; it is not hydroscopic, contains 68.21% uranium, and appears to be homogeneous according to X-ray structural studies.

On dissolving an aliquot of the compound $U_2O_3P_2O_7$ in 85% phosphoric acid on heating, a solution with a green color is obtained. By oxidimetric titration it was established that the compound contains 33.9% of the uranium in a quadrivalent state (mean of six determinations), i.e., half of the uranium present. In our opinion this compound is a pyrophosphate of quinquevalent uranium



which on dissolving in phosphoric acid dissociates into UO_2^{2+} and U^{IV}. The composition $(UO_2)_2P_2O_7\cdot(UO)_2P_2O_7$ with the same gross formula is less probable.



Thermogravimetric curve of ammonium uranyl phosphate.

Three series of experiments were carried out to determine the solubility product of $NH_4UO_2PO_4\cdot3H_2O$. In the first of these series (points 1-8) 1-g portions of $NH_4UO_2PO_4\cdot3H_2O$ at 25 ± 0.2° in 100-ml standard flasks, varying amounts of 0.1 N hydrochloric acid were added, and the volumes made up to the mark with water. In the second series of experiments (points 9-15), 10 ml of 0.1 M diammonium hydrogen phosphate solution was added in addition to each of the flasks. In the third series (point 16-20) the solid phase was obtained by pouring together solutions of uranyl nitrate and diammonium hydrogen phosphate. The flasks and their contents were shaken and the temperature thermostatted automatically until equilibrium was reached (72 hr). When equilibrium had been reached the solutions were filtered through a glass filter with a No. 4 porous disc. The uranium, phosphorus, and ammonium contents of the filtrates were determined as indicated above, while the pH was measured with a quinhydrone electrode using a PPTV-1 potentiometer. The results of some of the experiments (odd numbers) are given in Table 1.

TABLE 1. Experimental Results and Results of Calculations of the Solubility Product of $NH_4UO_2PO_4\cdot3H_2O$ at 25 ± 02°

Expt. No.	Equilibrium concentrations, moles/liter				Solubility product $P\cdot10^{-26}$
	uranium (C_1)	phosphate (C_2)	ammonium (C_3)	$[H^+]$	
1	$3,\ 0\cdot10^{-4}$	$1,53\cdot10^{-4}$	$2,\ 8\cdot10^{-3}$	$7,943\cdot10^{-3}$	3,28
3	$3,30\cdot10^{-3}$	$3,32\cdot10^{-4}$	$5,90\cdot10^{-3}$	$7,\ 08\cdot10^{-2}$	3,69
5	$7,20\cdot10^{-3}$	$7,23\cdot10^{-3}$	$7,79\cdot10^{-3}$	$1,349\cdot10^{-1}$	3,51
7	$1,15\cdot10^{-2}$	$1,13\cdot10^{-2}$	$1,13\cdot10^{-2}$	$1,950\cdot10^{-1}$	4,29
9	$2,80\cdot10^{-4}$	$1,00\cdot10^{-2}$	$2,04\cdot10^{-2}$	$6,\ 31\cdot10^{-2}$	4,56
11	$1,475\cdot10^{-3}$	$1,16\cdot10^{-2}$	$2,19\cdot10^{-2}$	$1,443\cdot10^{-1}$	2,83
13	$4,025\cdot10^{-3}$	$1,14\cdot10^{-2}$	$2,48\cdot10^{-2}$	$2,042\cdot10^{-1}$	2,88
15	$1,18\cdot10^{-2}$	$2,19\cdot10^{-2}$	$3,08\cdot10^{-2}$	$3,236\cdot10^{-1}$	5,14
17	$2,80\cdot10^{-3}$	$2,58\cdot10^{-3}$	$3,01\cdot10^{-2}$	$1,097\cdot10^{-1}$	3,45
19	$9,20\cdot10^{-3}$	$8,95\cdot10^{-3}$	$3,62\cdot10^{-2}$	$2,344\cdot10^{-1}$	5,02

In calculating the solubility product of ammonium uranyl phosphate, the following must be taken into account:

a) the hydrolysis of the uranyl ion (K_h = 6.4 · 10^{-5} [6]; its equilibrium concentration is calculated by means of the equation

$$[UO_2^{2+}] = \frac{C_1[H^+]}{K_h[H^+]};\tag{1}$$

b) dissociation of phosphoric acid through all its three stages ($K_1 = 7.51 \cdot 10^{-3}$, $K_2 = 6.23 \cdot 10^{-8}$, $K_3 = 4.8 \cdot 10^{-13}$); the equilibrium concentration of $[PO_4^{3-}]$ is calculated by means of the equation

$$[PO_4^{3-}] = \frac{C_2 \cdot K_1 \cdot K_2 \cdot K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}.\tag{2}$$

Hydrolysis of NH_4^+ over the pH range examined can be ignored.

Results of calculations of the solubility products by means of the equation

$$P = [NH_4^+][UO_2^{2+}][PO_4^{3-}] = \frac{C_1 \cdot C_2 \cdot C_3 \cdot K_1 \cdot K_2 \cdot K_3 \cdot [H^+]}{(K_r + [H^+])([H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}\tag{3}$$

are given in Table 1.

The mean value of the solubility product obtained as the result of a statistical treatment of 20 experiments proved to be equal to $P = (3.6 \pm 0.4) \cdot 10^{-26}$ at a confidence level of 0.95. The solubility of ammonium uranyl phosphate as a function of the pH of the solution, the concentrations of the phosphate ions ($C_2 = 1 \cdot 10^{-2}$M) and ammonium salts (C_3 = 1M) being constant, was calculated by means of equation (3). The solubility is characterized by the following results:

pH	2,0	3,0	4,0	5,0	7,0
C_1,,M	$2 \cdot 10^{-6}$	$2 \cdot 10^{-10}$	$3 \cdot 10^{-12}$	$1 \cdot 10^{-13}$	$2 \cdot 10^{-15}$

It follows from these results that quantitative precipitation of uranium as ammonium uranyl phosphate, under the conditions indicated, is possible in solutions having a pH greater than 3. Specially conducted experiments confirmed this assumption.

In weakly acid solutions (pH 3.0-5.0) the sparingly soluble phosphates of a number of other metal ions will be precipitated together with ammonium uranyl phosphate, but by introducing ethylenediaminetetracetic acid (H_4Y) it is possible to increase the selectivity of uranium separation significantly.

To determine the permissible concentration of interfering metallo-ion Me^{n+} (C_4,M) at which this ion will not be precipitated in the form of its phosphate at known pH values, concentrations of H_4Y (C_5,M), and phosphate concentration (C_2,M), the following processes must be taken into account:

$$Me^{n+} + H_2O = Me(OH)^{(n-1)+} + H^+, \qquad K_h = \ldots\tag{4}$$

$$H_3PO_4 = H_2PO_4^- + H^+, \qquad K_1 = 7{,}5 \cdot 10^{-3}\tag{5}$$

$$H_2PO_4^- = HPO_4^{2-} + H^+, \qquad K_2 = 6{,}3 \cdot 10^{-8}\tag{6}$$

$$HPO_4^{2-} = PO_4^{3-} + H^+, \qquad K_3 = 3{,}6 \cdot 10^{-13}\tag{7}$$

$$3Me^{n+} + nPO_4^{3-} = (Me_3)(PO_4)_n \qquad P = \ldots\tag{8}$$

In the pH range we are interested in, ethylenediaminetetracetic acid will exist in the form of the ion H_2Y^{2-}; accordingly, the following processes must be taken into account:

$$H_2Y^{2-} = HY^{3-} + H^+, \qquad K_4 = 6{,}92 \cdot 10^{-7}\,[7] \qquad (9)$$

$$HY^{3-} = Y^{4-} + H^+, \qquad K_5 = 5{,}47 \cdot 10^{-11}\,[7] \qquad (10)$$

$$Me^{n+} + Y^{4-} = MeY^{(4-n)-}, \qquad 1/K_6 = \ldots \qquad (11)$$

We denote the equilibrium concentrations as follows $[Me^{n+}] = x$, $[Me(OH)^{(n-1)+}] = y$, $[H^+] = h$, $[H_3PO_4] = V$, $[H_2PO_4^-] = W$, $[HPO_4^{2-}] = Z$, $[PO_4^{3-}] = U$, $[H_2Y^{2-}] = l$, $[HY^{3-}] = a$, $[Y^{4-}] = b$, and $[MeY^{(4-n)-}] = t$, M.

Applying the law of mass action to processes (4-11) and taking into account conversion of the original materials, we have:

$$K_h x = yh \quad (12) \qquad K_4 l = ah \quad (17)$$

$$K_1 V = Wh \quad (13) \qquad K_5 a = bh \quad (18)$$

$$K_2 W = Zh \quad (14) \qquad xb = K_6 t \quad (19)$$

$$K_3 Z = Uh \quad (15) \qquad C_4 = x + y + t \quad (20)$$

$$x^3 U^n \leqslant P \quad (16) \qquad C_5 = l + a + b + t \quad (21)$$

$$C_2 = V + W + Z + U \qquad (22)$$

To calculate C_4 from equations (17), (18), (19), and (21) we find $\underline{t}$

$$t = \frac{K_4 K_5 C_5 x}{K_4 K_5 x + (h^2 + K_4 h + K_4 K_5) K_6}. \qquad (23)$$

Substituting $\underline{t}$ from (23) in (20) and taking into account (12) and (16), we obtain:

$$C_4 \leqslant \frac{P^{1/3}}{U^{n/3}} \left[1 + \frac{K_h}{h} + \frac{K_4 K_5 C_5 x}{K_4 K_5 \dfrac{P^{1/3}}{U^{n/3}} + (h^2 + K_4 h + K_4 K_5) K_6} \right], \qquad (24)$$

where U is calculated from (13), (14), (15), and (22) by means of the equation

$$U = \frac{C_2 K_1 K_2 K_3}{h^3 + K_1 h^2 + K_1 K_2 h + K_1 K_2 K_3}. \qquad (25)$$

The inequality (24) enables one to evaluate the permissible concentration of interfering metallo-ion (C_4, M) at which it will not be precipitated as its phosphate, as a function of the concentration of hydrogen ions, excess precipitant, and original H_4Y concentration.

Results of calculations based on equation (24) are given in Table 2.

TABLE 2. Permissible Concentrations of Interfering Metallo-Ions at Which Selective Precipitation of $NH_4UO_2PO_4 \cdot 3H_2O$ Will Occur When $C_5 = 3.4 \cdot 10^{-2}$M, $C_2 = 1 \cdot 10^{-2}$M, as a Function of the pH of the Solution

Sparingly soluble compounds	Solubility product	Instability constant K_6 [8]	Permissible impurity concentration		Hydrolysis constant of the metallo-ion
			pH 3,0	pH 5,0	
$Ca_3(PO_4)_2$	$2{,}0 \cdot 10^{-29}$	$1{,}58 \cdot 10^{-11}$	7,9	$5{,}0 \cdot 10^{-2}$	$2{,}5 \cdot 10^{-13}$
$Mg_3(PO_4)_2$	$2{,}5 \cdot 10^{-13}$	$2{,}04 \cdot 10^{-9}$	$1{,}8 \cdot 10^{+6}$	$(3{,}7 \cdot 10^{+3})$	$2{,}0 \cdot 10^{-10}$
$Pb_3(PO_4)_2$	$7{,}9 \cdot 10^{-43}$	$9{,}12 \cdot 10^{-19}$	$3{,}4 \cdot 10^{-2}$	$3{,}4 \cdot 10^{-2}$	$3{,}3 \cdot 10^{-7}$
$Zn_3(PO_4)_2$	$9{,}1 \cdot 10^{-33}$	$3{,}16 \cdot 10^{-17}$	$6{,}5 \cdot 10^{-1}$	$3{,}5 \cdot 10^{-2}$	$2{,}5 \cdot 10^{-10}$
$AlPO_4$	$5{,}8 \cdot 10^{-19}$	$7{,}41 \cdot 10^{-17}$	$3{,}7 \cdot 10^{-2}$	$3{,}4 \cdot 10^{-2}$	$1{,}25 \cdot 10^{-5}$
$FePO_4$	$1{,}3 \cdot 10^{-22}$	$7{,}94 \cdot 10^{-26}$	$3{,}4 \cdot 10^{-2}$	$3{,}2 \cdot 10^{-2}$	$3{,}3 \cdot 10^{-3}$

The results given in Table 4 show that the method is applicable to the determination of uranium in its technical salts, oxides, concentrates, and alloys. Determinations can be carried out with reasonable accuracy and reliability.
their complete masking and ensure selective precipitation of uranium as ammonium uranyl phosphate.

On the basis of what has been said above, and on a whole series of preliminary experiments, the following technique is suggested for the preparation of a readily filterable precipitate of ammonium uranyl phosphate, and for subsequent gravimetric determination of uranium. An aliquot of test material is taken such that its uranium content is about 200-300 mg. Dissolution of aliquots of sodium uranyl acetate, uranium tetrafluoride, uranoso uranic oxide, uranium concentrates, uranium ores and alloys is carried out in nitric and hydrochloric acids, with subsequent evaporation of the solutions to 2-3 ml. In the case of alloys of uranium with zirconium, 10 ml of a 0.1% ammonium fluoride solution is added beforehand; decomposition is carried out as indicated above and then 10 ml of 30% tartaric acid solution added. The solutions obtained are diluted with water to 10-15 ml, heated to the boil, and filtered when necessary. The precipitate on the filter and the beaker are washed with a hot solution which is 5.5% with respect to ammonium chloride and 1% with respect to hydrochloric acid; 80-90 ml of this solution is used for washing. To the solutions obtained is added 10 ml of 10% NH_4ethylenediaminetetracetate solution. When test materials contain a large amount of aluminum, the amount of NH_4ethylenediaminetetracetate added is equivalent to the stoichiometric amount necessary for complexing all the aluminum plus 5-10 ml in excess. The solution is next heated to the boil and 0.2 M diammonium hydrogen phosphate added until a precipitate appears. The liquid is boiled for one minute and an additional amount of ammonium phosphate solution added until the total volume is 10 ml. After 5 min, 0.6-0.8 ml of a 0.1% aqueous solution of alizarin red is added; this is followed by ammonia solution (1-3) until a rose color appears (pH 3.7-5.2). After 5-10 min the solution is decanted onto a white band filter paper; the precipitate is transferred onto the filter paper and washed with hot 2% ammonium chloride solution containing 0.1% ammonium ethylenediaminetetracetate. 80-170 ml of wash liquor is used for each precipitate. The precipitates are placed in tared crucibles; the filter papers are ashed, and the whole calcined at 900-1000° for one hour; the residue is finally weighed as $U_2O_3P_2O_7$. A blank is carried out in parallel, and the weight of the filter paper ash subtracted from the weight obtained. Results of a check on the method using synthetic mixtures are given in Table 3. A standard solution of uranyl nitrate and aqueous solutions of the salts of the corresponding elements were used for these experiments.

TABLE 3. Results of Statistical Treatment of Experimental Results on Determination of Uranium in Solutions Containing Impurities

Added				No. of uranium determinations	Uranium found, mg	Mean square error	
uranium, mg	impurity, mg	H_4Y, g	tartaric acid, g			mg	% (relative)
286,6		1,0	—	12	286,6	±0,30	±0,10
286,6	$20Fe^{3+}$, $20Al^{3+}$, $20V^{5+}$, $20Na^{+}$	2,5	—	12	286,9	±0,58	±0,20
241,7	35 Cr^{3+}	1,5	—	10	241,7	±0,12	±0,05
241,7	35 Zr^{4+}	1,0	3,0	11	241,9	±0,15	±0,06
241,9	24 0 Al^{+3}	4,5	—	11	241,9	±0,13	±0,06

The results given in Table 3 show that the method gives correct and readily reproducible results for uranium determination. The loss of uranium with the filtrates, as determined by luminescent analysis, does not exceed 0.1 mg. It should be pointed out that in the presence of chromium, during adjustment of the requisite pH, the indicator changes its color from yellow to red-violet, while in the presence of tartaric acid it changes from yellow to orange.

Determination of uranium in actual test materials (Table 4) is carried out as indicated in the procedure outlined above.

The results given in Table 4 show that the method is applicable to the determination of uranium in its technical salts, oxides, concentrates, and alloys. Determinations can be carried out with reasonable accuracy and reliability.

One analyst can carry out 10-12 uranium determinations in six hours.

TABLE 4. Results of a Check on the Method

Test material	Uranium content, %	Suggested method			
		no. of determinations	uranium found, %	mean square error	
				% (absolute)	% (relative)
Sodium uranyl acetate	50,76	11	50,80	±0,13	±0,25
Uranoso uranic oxide	82,91	11	82,99	±0,16	±0,19
Uranium tetrafluoride	72,51	11	72,77	±0,16	±0,22
Concentrate	51,60	11	51,59	±0,16	±0,31
Ore	15,26	12	15,40	±0,10	±0,60
Alloy with Zr	89,61	12	89,80	±0,11	±0,13
Alloy with Al	70,15	11	70,24	±0,14	±0,20

SUMMARY

The solubility product of ammonium uranyl phosphate $NH_4UO_2PO_4 \cdot 3H_2O$ has been determined. It was found to be equal to $(3.6 \pm 0.4) \cdot 10^{-26}$ at 25°.

A gravimetric method has been developed for the determination of uranium; it is based on precipitation of ammonium uranyl phosphate in the presence of ammonium ethylenediaminetetracetate, and weighing the uranium as $U_2O_3P_2O_7$.

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THE USE OF C_7-C_9 FATTY ACID FRACTION FOR SEPARATION OF IRON AND COPPER FROM COBALT

S. E. Kreimer, N. V. Tuzhilina, L. M. Gaeva, and A. S. Lomekhov
"Severonikel' " Combine, Monchegorsk

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Photometric determination of small amounts of cobalt by means of nitroso-R-salt in materials containing large amounts of iron, copper, nickel, and chromium is a problem which has hitherto proved difficult and has attracted the attention of rearch workers. Determination of about 0.5% cobalt can be carried out by this method without separating it from the other elements in the presence of up to 70% iron, 5% nickel, and 15% copper [1,2]. During cobalt determination some authors have masked iron with sodium fluoride or phosphoric acid [3]. In order to increase the accuracy of determination of small amounts of cobalt in steels and iron, iron has been separated by extraction with isopropyl ether or in the form of its complex with cupferron [4,5]. Diantipyrylmethane has been used for separating cobalt from nickel, manganese, chromium, zinc, cadmium, magnesium, barium, and calcium [6]. Copper can be separated from cobalt by means of lead diethyldithiocarbamate [7,8]. For the analysis of ores containing large amounts of iron and copper, copper has been separated with potassium nitrite. A colorimetric finish with nitroso-R-salt is used. The method is very tedious and takes a long time. Despite this, the method is widely used at present [9]. Gindin et al.[10] have for technological purposes, suggested separation of iron and copper from cobalt by means of a mixture of saturated acids with carbon numbers 7 to 9. Kuznetsov has shown that the extractability of copper salts of fatty acids increases with increasing hydrocarbon chain length [11]. Extraction of copper salts of fatty acids for the quantitative determination of copper has been described [12].

The present article is devoted to a description of a method for the photometric determination of cobalt by means of nitroso-R-salt after separation of cobalt from iron by means of fatty acids, and from copper by means of lead diethyldithiocarbamate. Diantipyrylmethane is used for separating cobalt from nickel and a number of other elements.

Extraction of Iron and Copper with a Fatty Acid Mixture. A 20% solution of a mixture of C_7-C_9 fatty acids in chloroform was used for extraction.

The iron alum and cupric sulfate solutions used contained about 0.004 g Fe per ml and about 0.004 g Cu per ml respectively. Buffer mixtures were prepared by mixing 0.2 N solutions of acetic acid and sodium acetate.

The fatty acid mixture is produced by the Combine of Synthetic Fatty Acids and Higher Alcohols, Shebekino, according to GOST 8622-57.

Five ml of the iron or copper salt solution, 50 ml of buffer mixture, and 55 ml of the fatty acid solution were introduced into a 200-ml separating funnel. Extraction was carried out for 2 min. After the layer had separated, the organic layer was poured into another separating funnel and copper and iron extracted into the aqueous phase, extraction being carried out twice with 20-ml lots of hydrochloric acid (1 : 4) for one minute. Iron was determined in the acid extract iodometrically after its precipitation with ammonia and subsequent dissolution of the hydroxide; copper was precipitated with thiosulfate after evaporation of the acid extract with sulfuric acid until all the chlorides had been removed; the determination was finished iodometrically.

Results of experiments on extraction of copper and iron are given in Table 1.

The results given in Table 1 show that extraction of iron and copper from acetic acid solutions is almost complete at pH values close to those for the precipitation of the hydroxides of these metals; this is in agreement with published results [10].

Palmitic acid (m.p. 64°) was also tested as an extractant. Four g of powdered palmitic acid was scattered into a beaker containing the iron or copper salt solution; the mixture was then heated to the boil and boiled for 2 min. After cooling, the solution and the reextract obtained by boiling the solidified palmitic acid with hydrochloric acid were analyzed.

TABLE 1. Relation between Extraction of Iron and Copper with Fatty Acids and the pH of the Aqueous Solution (22.2 mg iron and 20.2 mg of copper were taken in all the experiments)

pH of the aqueous solution	Iron found in the reextract, mg	Iron extracted, %	Copper found in the reextract, mg	Copper extracted, mg	Separation of iron and copper			
					found in the aqueous solution after extraction		found in the reextract	
					iron, mg	copper, mg	iron, mg	copper, mg
3,7	8,5	38,3	5,6	27,7	15,9	20,2	6,0	Trace
4,3	22,2	100	15,1	74,7	0,3	19,3	21,5	0,8
4,6	22,2	100	18,6	92,1	0,3	8,0	21,3	12,2
5,0	22,2	100	19,8	98,0	0,2	3,4	21,5	16,7
5,4	22,1	100	20,0	99,0	0,2	2,2	21,3	18,1
5,6	22,1	99,5	20,0	99,0	0,3	0,9	21,2	18,8

TABLE 2. Separation of Trivalent Iron from Cobalt in Sulfuric Acid Solutions

20 mg iron taken*		1000 mg iron taken		1000 mg iron taken**	
Cobalt, mg					
taken	found	taken	found	taken	found
0,01	0,011	0,02	0,02	0,02	0,021
0,02	0,02	0,04	0,04	0,04	0,043
0,03	0,03	0,06	0,059	0,06	0,06
0,04	0,039	0,08	0,08	0,08	0,08
0,05	0,05	0,10	0,10	0,10	0,099
0,06	0,057				
0,07	0,068				
0,08	0,074				

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* Iron alum solution (the preparation contained 0.002% cobalt).

** Ferric sulfate solution prepared from Armco iron containing 0.014% cobalt.

These experiments showed that extraction does not depend to a significant extent on the length of the hydrocarbon chain, at a fixed pH.

Separation of Cobalt from Iron, Copper, and Other Metals. It was established that cobalt is not extracted with the chloroform solution of fatty acids at pH 5.6, the optimum pH for separation of iron and copper.

Solutions of iron and copper salts, and a cobalt sulfate solution containing 0.00001 g Co per ml were introduced into a separating funnel. A 50% solution of sodium acetate was added dropwise until the pH was about 5 according to universal indicator paper. Thirty ml of buffer solution (pH 5.6) and 50-100 ml of the 20% solution of fatty acids in chloroform were added, and the whole shaken for 1-2 min; extraction was repeated until a colorless organic phase was obtained. The aqueous layer was washed free from fatty acids by shaking with pure chloroform. The aqueous layer was transferred to a 250-ml conical flask,and 20 ml of 50% sodium acetate was added; the mixture was heated to the boil and then evaporated to reduce its volume; 10 ml of 0.5% nitroso-R-salt solution was added and the liquid boiled for one minute; 25 ml of nitric acid (1 : 1) next was added and the liquid again boiled for one minute; it was finally cooled and transferred to a 200-ml standard flask.

Calibration curves were constructed using pure cobalt sulfate solutions, the extraction step being omitted.

Results of experiments on the separation of iron from cobalt are given in Table 2. The optical density was measured relative to the "blank" solutions obtained after extracting the iron. 1000 mg of iron can be separated by carrying out two extractions with 100- to 120-ml lots of the fatty acid solution.

TABLE 3. Separation of Copper from Cobalt with Lead Diethyldithiocarbamate

Copper taken, mg	Cobalt, mg		Copper taken, mg	Cobalt, mg	
	taken	found		taken	found
10	0,02	0,02	100	0,02	0,02
10	0,04	0,04	100	0,04	0,04
10	0,06	0,061	100	0,06	0,06
10	0,08	0,081	100	0,08	0,08
			1000	0,04	0,038
			1000	0,08	0,083

TABLE 4. Separation of Iron and Copper from Cobalt by means of Lead Diethyl dithiocarbamate and the Fatty Acids in Nitric Acid Solutions

20 mg copper and 20 mg iron taken		100 mg copper and 100 mg iron taken	
Cobalt, mg			
taken	found	taken	found
0,02	0,023	0,02	0,02
0,04	0,038	0,04	0,039
0,06	0,059	0,06	0,061
0,08	0,078	0,08	0,081

Experiments showed further that complete separation of 400 mg of copper is only achieved after 10-12 extractions, although the bulk of the copper is extracted during the first operation. Accordingly, we checked on the possibility of separating copper with a solution of lead diethyldithiocarbamate in chloroform (4.5 g lead per liter). To 50 ml of cupric nitrate solution prepared from electrolytic copper (free from cobalt) was added cobalt sulfate solution and 50 ml of acetate buffer mixture (pH 4.1). The experimental results are given in Table 3.

It follows from these results that lead diethyldithiocarbamate completely separates copper from cobalt. The lead which passes into the aqueous solution does not interfere with the photometric determination of cobalt with nitroso-R-salt.

Table 4 contains the results for the separation of iron and copper from cobalt. Copper was extracted at pH about 3 with a solution of lead diethyldithiocarbamate in chloroform; the pH was then adjusted to 5.6 by addition of acetate buffer mixture and the iron extracted with a solution of the fatty acid mixture in chloroform. Iron and copper salts were added in the "blank" experiments.

The method described for separating iron and copper gives considerably worse results in sulfuric acid solutions, since the lead which passes into the aqueous phase is precipitated as $PbSO_4$.

Results of experiments with sulfuric acid solutions carried out as follows proved satisfactory. Iron and the bulk of the copper were extracted with the fatty acids at pH about 5, and the residual copper was extracted with lead diethyldithiocarbamate at pH about 4. Under these conditions, the amount of lead which passes into solution is small, and in the presence of acetic acid and sodium acetate a precipitate of $PbSO_4$ is not formed. During determination of 0.02, 0.04, 0.06 and 0.08 mg Co, the amounts of cobalt found were 0.02, 0.04, 0.06 and 0.08 mg respectively.

Salts of trivalent chromium and divalent maganese are not extracted by the chloroform solution of fatty acids over the pH range 3.7-7.9.

Separation of small amounts of cobalt from large amounts of nickel by means of the fatty acids is not feasible. Accordingly, in order to separate cobalt from trivalent chromium, divalent manganese, and nickel, we made use of the extraction of cobalt in the presence of ammonium thiocyanate and diantipyrylmethane [6].

Analysis of Steels and Ores. An aliquot of the solution of test material is transferred to a 250-ml separating funnel; 50% sodium acetate is added dropwise until the pH is about 5 (a drop of solution is placed on the indicator paper through a double layer of filter paper since the solution has a red color); this is followed by 30 ml of acetate buffer mixture (pH 5.6). One hundred ml of the 20% solution of fatty acids in chloroform is added and the whole shaken vigorously. Extraction is repeated until a colorless organic layer is obtained; the aqueous layer is then washed with 10 ml of chloroform; the solution is acidified with hydrochloric acid until the pH is 3-4, and the remaining copper extracted with a solution of lead diethyldithiocarbamate in chloroform. The aqueous layer is washed with about 10 ml of chloform and is poured into a 250-ml conical flask. The solution is heated to the boil and 20 ml of 50% sodium acetate solution added; 10 ml of a 0.5% solution of nitroso-R-salt is added to the boiling solution and the whole boiled for one minute; 25 ml of nitric acid (1: 1) is added and the solution boiled again for one minute; it is finally cooled and transferred to a 200-ml standard flask.

When the sample contains large amounts of nickel, chromium, and manganese, the solution left after removal

TABLE 5. Determination of Cobalt in Steel (Cobalt Found in the Sample 0.016%) Sample wt. 0.2 g; Sulfuric Acid Solution

Cobalt, mg	
Taken	Found
0.04	0.039
0.07	0.071
0.10	0.099

of the iron and copper is acidified with hydrochloric acid until the pH is 1-2 according to universal indicator paper; 10 ml of a 40% ammonium thiocyanate solution and 20 ml of a 2% solution of diantipyrylmethane in 0.5 N HCl are added and shaken for 1 min, and the Co compound extracted with 10 ml of chloroform. This operation is repeated twice. When the cobalt content is high the extract is colored blue by the cobalt complex. To the organic layer contained in a separating funnel is added 20 ml of a 0.2 N sodium acetate solution and 5 ml of 0.5% nitro-R-salt solution, and the whole shaken for one minute; the organic layer is transferred to another separating funnel, while the aqueous layer is transferred to a 200-ml standard flask. Twenty ml of 0.2 N sodium acetate and 5 ml of 0.5% nitroso-R-salt solution are added again to the organic layer. After shaking, the aqueous layer is transferred to the standard flask, while the chloroform is discarded. To the aqueous solution in the standard flask is added 10 ml of nitric acid (1 : 1), and the liquid is left for 15 min. The volume is made up to the mark with water and the optical density of the solution is measured on a FÉK-M photoelectric colorimeter fitted with a green filter.

TABLE 6. Determination of Cobalt in Ores

Co found by the method suggested, %		Co found photometrically after its isolation as cobaltinitrite
Determination I	Determination II	
0.040	0.042	0.041
0.034	0.034	0.032
0.042	0.042	0.042
0.052	0.054	0.052
0.031	0.032	0.032
0.152	0.150	0.157
0.180	0.181	0.181
0.059	0.058	0.058

The "blank" solution is prepared by adding sodium acetate, nitroso-R-salt, and nitric acid to water.

A calibration curve is constructed using cobalt sulfate solution; the extraction operation is omitted.

The method has been checked by adding known amounts of cobalt to a standard sample of No. 53-a steel, containing 12.1% Cr. The optical density was measured relative to a "blank" solution obtained from an aliquot of steel to which no cobalt was added. The experimental results are given in Table 5.

Table 6 contains the results of cobalt determination in ore products containing large amounts of copper. Samples chosen for analysis were ones to which photometric determination by means of nitroso-R-salt was inapplicable without preliminary separation of cobalt. The agreement between the results obtained justifies the technique of separating cobalt by extraction.

SUMMARY

The use of a solution of C_7-C_9 fatty acids in chloroform, and of a solution of lead diethyldithiocarbamate in chloroform, is suggested for separating small amounts of cobalt from large amounts of iron and copper. A method which has been developed has been checked on synthetic solutions, steels, and ores.

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POTENTIOMETRIC DETERMINATION OF COBALT WITH FERRICYANIDE IN A GLUTAMIC ACID MEDIUM

Chang Yeh Siya, J. Doležal, and J. Zýka
Charles University, Prague (Czechoslovakia)

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Quantitative oxidation of divalent cobalt in the form of its glutamate complex by mean of potassium ferricyanide has been studied potentiometrically as a function of pH and the concentration of glutamic acid and cobalt. It was established in the course of this work that the compound of divalent cobalt with glutamic acid is stable in air at a pH of 9.8-11.4, and that it is possible to oxidize it quantitatively with potassium ferricyanide. As a result of the present investigation a method has been developed for the determination of cobalt in various materials (steel, ores). The method permits determination of 1% Co in zinc, nickel, bismuth, cadmium, copper, and molybdenum. Manganese in amounts which are five times that of cobalt does not interfere.

Potassium ferricyanide is used as an oxidizing agent for the determination of cobalt in an ammoniacal medium [1-2]. Since low results are obtained during direct titration, the normal procedure is to add a solution of the sample to a standard ammoniacal solution of ferricyanide, excess of the latter being then back-titrated with a standard cobalt salt solution. The interaction of cobalt salts with ferricyanide has been studied by many authors [3-5]; Diehl and Butler [6] have replaced ammonia by ethylenediamine, which ensures more favorable conditions for carrying out titration.

Oxygen, however, readily oxidizes the ethylenediamine complex of divalent cobalt, so that it is necessary to work in an inert atmosphere. Kopanica and Doležal [7] eliminated this drawback by using glycine.

Titration with ferricyanide is the best method for determining cobalt and is characterized by high selectivity. Ways of eliminating interference from manganese have been indicated in previous articles. It has been shown that it is possible to determine manganese together with cobalt in a medium of ethylenediamine and sulfosalicylic acid [6]. The polarographic behavior of the complex salts of cobalt with glutamic acid has been studied in detail [8], as well as the oxidation of this stable compound with ferricyanide. In the present article the possibility is demonstrated of determining cobalt potentiometrically in air with potassium ferricyanide in the presence of glutamic acid. The method has given very good results during analysis of various steels and ores and is suitable as a simple method and for industrial control. Glutamic acid is readily available and is not an expensive reagent.

METHOD

Reagents: A 0.1 N solution of potassium ferricyanide was prepared from a Czech product (LAKhEMA) and was checked iodometrically. More dilute solutions were prepared by diluting the 0.1 M solution.

A standard cobalt sulfate solution was prepared from the pure product ($CoSO_4 \cdot 7H_2O$, Merck); Co concentration was established electrolytically.

The glutamic acid used was a Czech product (VITANA). The dissociation constants of glutamic acid which are given in the literature ($pH_1 = 2.19$, $pK_2 = 4.25$, $pK_3 = 9.66$ and $pK_1 = 2.16$; $pK_2 = 4.32$, $pK_3 = 9.96$), were checked by potentiometric titration with sodium hydroxide using a glass indicator electrode. The results obtained for pK_2 and pK_3 are in almost complete agreement with published results [9-13] (the pK values found were 2.3, 4.30, and 9.60). The value of pK_1 cannot be determined accurately from the titration curve (Fig. 1).

The samples of steel used conformed to international standards.

Potentiometric titration with ferricyanide was carried out on a "KRATO" instrument (Kratovkhvil Engineering School, Prague). A "Multoscope" apparatus (Laboratory Apparatus, Prague) was used for measuring the pH.

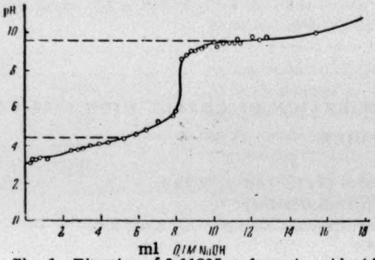

Fig. 1. Titration of 0.11205 g glutamic acid with 0.1 M NaOH (φ = 0.9747).

RESULTS

Data on the complexes of glutamic acid with metal ions have been published by many authors; these include complexes with Co^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} [14-16], and with Cu^{2+} in an alkaline medium (polarographically [17-18] and potentiometrically [19]). The complexes of Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+} [20,21], as well as those of Ag^{+} [22,23] and the rare earths [24] have also been studied polarographically and by oscillographic polarography.

Glutamic acid interacts with Co^{2+} in the proportion of 2:1 [15,16,25].

The compound of cobalt with glutamic acid does not change in air, but it is oxidized by potassium ferricyanide.

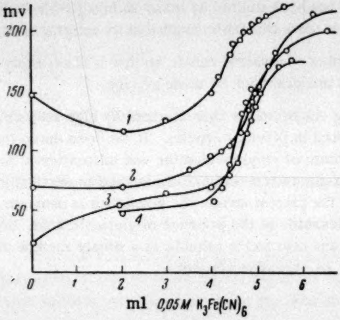

Fig. 2. Effect of pH on the oxidation of the divalent cobalt complex of glutamic acid with ferricyanide. 5 ml of 0.05 M $CoSO_4$ in 50 ml of 0.2 M glutamic acid. Theoretical amount required: 4.94 ml of 0.05 M $K_3Fe(CN)_6$.

Effect of pH on Oxidation of Cobalt in a Glutamic Acid Medium. The bright red colored complex of cobalt with glutamic acid is formed over a fairly wide pH range. It is oxidized to a violet colored complex even at ordinary temperatures. The course of the oxidation reaction was followed quantitatively by titrating about 15 mg Co^{2+} with 0.05 M potassium ferricyanide, titration was carried out in 50 ml of 0.2 M glutamic acid at a definite pH. Fig. 2 shows the course of the reaction. Titration can be carried out over the pH range 4.3-12.5. At a pH greater than 7 partial separation of a precipitate occurs, while in solutions with pH greater than 12.5 it becomes impossible to establish the position of the titration end point. At pH values greater than 11.5, after about 15 min, the color of the solution gradually starts to change and a brown color appears.

It is clear from Fig. 2 that as the pH increases the initial potential of the solution starts to decrease gradually. On Curve 1 there is observed a further potential drop after the first addition of potassium ferricyanide solution. Quantitative oxidation occurs over the pH range 9.8-11.4. The potential is readily established in all cases in the immediate neighborhood of the titration end point (within 2 min), independently of the pH. The potential jump at the end point does not change strongly, but is strong enouth to establish the titration end point reliably.

At pH's within the optimum range there is no need to protect the solution being titrated from contact with atmospheric oxygen (Fig. 3). Even after solution has been allowed to stand for $3\frac{1}{2}$ hours, oxidation of cobalt is negligible.

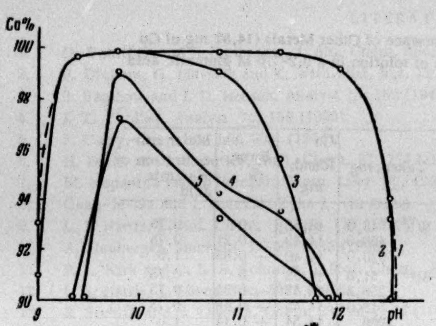

Fig. 3. Titration of the complex of Co^{2+} with glutamic acid in the absence and in the presence of atmospheric oxygen. 1) Immediately in an inert atmosphere; 2) immediately in air; 3) in the air after 3.5 hr; 5) in the air after 5 hr; 5) in the air after 12 hr.

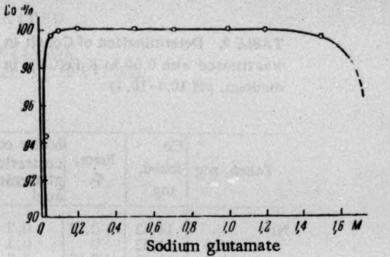

Fig. 4. Effect of glutamic acid concentration on oxidation of divalent cobalt with potassium ferridyanide; 4.5×10^{-3}M Co^{2+} solution was titrated with 0.05 M $K_3Fe(CN)_6$ at pH 10.4 in a volume of 55 ml.

Effect of Glutamic Acid Concentration. Even in the presence of a tenfold amount (with respect to cobalt) of glutamic acid, the potential change at the titration end point is only 2-3 mv for 0.1 ml of $K_3Fe(CN)_6$. As the amount of glutamic acid used increases so does the potential jump. When the amount of glutamic acid is 40-240 times as much as that of the cobalt the potential changes by 20-50 mv on addition of 0.1 ml of ferricyanide solution.

When very large amounts of glutamic acid are used (more than 250-fold) low results are obtained for cobalt (at pH 10.4, Fig. 4).

Under the optimum conditions, i.e., at pH 9.8-10.4 and a glutamic acid concentration of 0.2 M, and using a volume of 50 ml of solution, it is possible to determine 1.5-50 mg of cobalt with reasonable accuracy (Table 1). At higher cobalt concentrations it is necessary to increase the amount of glutamic acid.

Effect of Other Ions. Chlorides, nitrates, and sulfates in amounts which are 50-100 times that of cobalt do not affect the results of cobalt determination. A number of cations form colorless (Mo^{VI}, Bi^{3+}, Zn^{2+}, Mn^{2+}) or colored (Fe^{3+} intense yellow-red, Cu^{2+} intense bluish-violet, VO_3 bright yellow, Ni^{2+} intense blue) compounds with glutamic acid, but even when these elements are present in large amounts they do not affect the results of cobalt determination (Table 2); the exception is manganese.

TABLE 1. Titration of Divalent Cobalt in a Glutamic Acid Medium with Potassium Ferricyanide Solution (pH 9.8-10.4, mean of three determinations)

Co taken, mg	Co found, mg	Co taken, mg	Co found, mg
1.45	1.39*	14.52	14.52**
2.90	2.85*	21.80	21.80**
7.26	7.26**	29.00	29.00**

* Titrated with 0.01 M $K_3Fe(CN)_6$.

** Titrated with 0.05 N $K_3Fe(CN)_6$.

When manganese compound is added on its own to a glutamic acid solution (pH 10.4), as soon as the first drop of $K_3Fe(CN)_6$ solution is added, a greenish-brown colored precipitate appears, and the measured potential value corresponds to the potential value of the system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. When, however, the solution contains cobalt as well as manganese, the precipitate of the maganese compound only appears after complete oxidation of divalent cobalt. The compound of manganese with glutamic acid is not oxidized by atmospheric oxygen, in contrast to the compound of manganese with glycine [7]. Quantitative results were obtained for cobalt in the presence of 1.5 times its amount of manganese.

Determination of Cobalt in Steel. About 0.5 g of steel containing Cr, Mo, W, and V in addition to cobalt is dissolved in perchloric acid and the solution evaporated almost to dryness. The residue is dissolved in distilled water containing a small amount of perchloric acid and the liquid heated to separate the tungstic acid. Solution and precipitate are transferred to a 100-ml standard flask and the volume made up to the mark with distilled water. 25 ml of 60% glutamic acid solution (pH 10.1-10.5) is added to 25 ml of this solution and the final solution titrated

TABLE 2. Determination of Cobalt in the Presence of Other Metals (14.52 mg of Co was titrated with 0.05 M $K_3Fe(CN)_6$ in 50 ml of solution in a 0.2-1.5 M glutamic acid medium, pH 10.1-10.4)

Taken, mg		Co found, mg	Error, %	Molar concentration of glutamic acid	Taken, mg		Co found, mg	Error, %	Molar concentration of glutamic acid
Ni^{2+}	—	14,53	+0,07	0,2	W^{VI}	46,0	14,52	0	0,75
	14,6	14,52	0	0,2		460,0	14,49	— 0,21	0,75
	58,4	14,53	+0,07	0,2		920,0	14,40	— 0,83	1,5
	116,8	14,45	—0,48	0,2	Bi^{3+}	51,8	14,52	0	0,75
	101,3	14,50	—0,14	0,75		258,3	14,47	— 0,34	0,75
	202,6	14,51	—0,07	1,5		518,0	14,45	— 0,48	0,75
Cr^{3+}	10,288	14,53	+0,07	1,5		1036	14,54	+ 0,14	1,5
	20,567	14,50	—0,14	1,5	Ti^{IV}	9,99	14,49	— 0,21	0,5
	51,42	14,35	—1,17	1,5		4,99	14,51	— 0,07	0,5
	102,80	14,20	—2,2	1,2	Mo^{VI}	3360	14,45	— 0,48	0,75
Cd^{2+}	140,3	14,49	—0,21	1,2		1680	13,30	— 1,51	0,5
	280,5	14,42	—0,69	1,2		504	14,51	— 0,07	0,5
	280,5	14,51	—0,07	1,5		840	14,49	— 0,21	1.5
	561,0	14,28	—1,67	1,2		840	1,33	—70,7	0,25
Al^{3+}	13,42	14,52	0	1,2	VO_3^-	6,10	14,52	0	0,5
	33,55	14,35	—1,17	1,2		21,8	14,57	+0,342	0,5
	67,10	14,35	—1,17	1,2		109,0	14,57	+0,21	0,5
Fe^{3+}	139,85	14,48	—0,28	1,2	As^V	141,2	14,55	+0,21	0,5
	139,85	14,53	+0,07	1,5		282,4	14,51	—0,07	0,5
	279,7	14,47	—0,34	1,5	Mn^{2+}	5,48	14,53	+0,07	0,5
Cu^{2+}	194,0	14,51	—0,07	1,5		8,22	14,51	—0,07	0,5
	382,0	14,50	—0,14	1,5		13,70	14,49	—0,21	0,5
Zn^{2+}	162,5	14,52	0	1,2		27,40	14,55	+0,21	1,1
	325,0	14,49	—0,21	1,5		68,5	14,43	—0,62	1,1

pontentiometrically with 0.05 M potassium ferricyanide solution. The mean cobalt content from several determinations was found to be 4.15% (amount that should be present, 4.52%). In another steel the cobalt content found was 2.05%, the amount that should be present being 1.95%.

Determination of Cobalt in an Ore. About 1 g of finely ground arsenic sulfide ore (Co, Ni, As) is dissolved in perchloric acid and the solution evaporated to dryness; the residue is dissolved in water containing a few drops of sulfuric acid. The evaporation process is repeated and the solution transferred with water containing a few drops of perchloric acid into a 250-ml standard flask, water being added to bring the volume up to the mark. To 25 ml of the solution obtained as is added 25 ml of 60% glutamic acid solution (pH 10.5), and the cobalt is titrated potentiometrically with 0.1 M $K_3Fe(CN)_6$. As the result of a large number of determinations the mean cobalt content of a sample which was supposed to contain 0.66% was found to be 0.67%.

On the basis of a large number of determinations carried out on a cobalt-nickel ore, the mean cobalt content found was 0.56% Co as against an expected content of 0.51% Co.

SUMMARY

The quantitative oxidation of divalent cobalt as the divalent cobalt complex of glutamic acid by means of potassium ferricyanide has been studied potentiometrically as a function of pH, glutamic acid and cobalt concentrations. It has been found that the cobalt (II)-glutamic acid compound is stable in air at pH 9.8-11.4, and it is possible to oxidize it quantitatively with potassium ferricyanide. As a result of the studies carried out, a method has been developed for the determination of cobalt in various materials (steels, ores). The method permits determination of 1% Co in zinc, nickel, bismuth, cadmium, copper, and molybdenum. Manganese in amounts which are five times that of cobalt does not interfere.

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NITROPHENYLHYDRAZONES OF ISONITROSOACETOPHENONE AS SENSITIVE AND SELECTIVE REAGENTS FOR COBALT*

G. S. Deshmuk, V. D. Anand, and K. N. Mekrotra

Benares Hindu University (India)

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Isonitrosoacetophenone has been used for a long time as a reagent for detecting iron [1-3], cobalt, nickel, cadmium, copper, lead, tin, zinc, and mercury [4]. With these elements the reagent forms inner-complex salts with characteristic colors. Recently, the p-nitrophenylhydrazones of certain isonitroso compounds (e.g., isonitrosoacetone and 3-isonitrosopentanedione [5] were suggested as selective reagents for cobalt. A hydrazone is readily formed as the result of the presence of a free keto group in isonitrosoacetophenone. It was of interest to study the effect of the introduction of an aromatic group on the reactivity of the group for cobalt. In this connection we synthesized the p-nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone and studied their analytical behavior.

Synthesis of Reagents. a) p-Nitrophenylhydrazone of isonitrosoacetophenone. 1.5 g of p-nitrophenylhydrazine in 100 ml hot water was added to a solution of 1.5 g of isonitrosoacetophenone (chemically pure grade, Theodore Shuchardt) in 25 ml of hot water. The mixture was acidified by addition of a few drops of glacial acetic acid and was kept on a boiling water bath for 25-30 min. After cooling, the orange precipitate was filtered off; it was recrystallized from methanol. The preparation obtained was a dark-orange powder with m.p. 212°. Analysis **:

Found (in %):	58.78 C;	4.39 H;	18.85 N.
$C_{14}H_{11}N_4O_3$. Calculated (in %):	59.15 C;	4.23 H;	18.72 N.

b) 2,4-Dintrophenylhydrazone of isonitrosoacetophenone. Equimolar amounts of isonitrosoacetophenone and 2,4-dinitrophenylhydrazine were mixed in hot dilute alcohol, and the mixture was acidified with acetic acid and heated under reflux for 3-4 hr. On cooling, a dark-red precipitate was obtained. The precipitate was recrystallized from toluene. The preparation obtained was a red crystalline powder with a m.p. of 233°. Analysis:

Found (in %):	51.28 C;	3.26 H;	20.50 N.
$C_{14}H_{10}N_5O_5$. Calculated (in %):	51.06 C;	3.34 H;	21.28 N.

Detection of Cobalt. A 0.1% solution of the reagents in ethanol was used.

To one drop of test solution contained in a micro test tube was added one drop of concentrated ammonia and two drops of the alcoholic solution of the reagent. Depending on the amount of cobalt, a dark or light violet color develops. When very small amounts of cobalt are present a rose color develops, and in such cases the color is observed after removing excess unreacted reagent by extraction with ether.

When the p-nitrophenylhydrazone of isonitrosoacetophenone is used the limit of identification is 0.1 μg, while the limiting dilution is 1:2 000 000. When the 2,4-dinitrophenylhydrazone of isonitrosoacetophenone is used, a dark-red color appears; the limit of identification is 0.25 μg Co, while the limiting dilution is 1 : 1 000 000.

Nickel at high concentrations gave a light-blue color, which can be eliminated by addition of a dilute solution of an alkali metal cyanide. A large excess of cyanide should be avoided since it interferes with cobalt detection. Other cations which form soluble ammines, e.g., silver, copper, and palladium, did not give a color with the reagents. The color which develops in the presence of cobalt was stable in the presence of a moderate excess of KCN and ammonium salts.

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* Translated from English by Z. I. Podgaiskaya.

** Analysis was carried out by Doctors Wiler and Straus (Oxford, England).

Cadmium, iron, lead, manganese, mercury, tin, and zinc (they give color reactions with isonitrosoacetophenone) do not interfere with cobalt detection.

Both reagents are soluble in solutions of the alkali metal hydroxides, since they are enolizing nitroso compounds, to form acidonitro compounds as a result of a regrouping. Both reagents also possess acid properties since they contain an oxime group with a hydrogen atom which is capable of forming a coordination bond with nitrogen. The transformation into the ionogenic quinoid form,which is soluble in alkalis, can be explained in the same way as in the case of the p-nitrophenylhydrazones of isonitrosoacetone and 3-isonitrosopentanedione [5].

This regrouping does not proceed fully enough in the presence of ammonia, so that only a bright-orange color developed.

When cobalt and ammonia are present, regrouping of the reagent molecules occurs with simultaneous complexing of cobalt as a chelate compund.

Formation of the violet complex compounds of cobalt with the p-nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone, which are stable to alkali metal cyanides, can be used as a new and fairly sensitive reaction for cobalt. The ordinary cations do not interfere. The introduction of the phenylhydrazone group into isonitrosacetophenone essentially modifies the nature of the reagent, as a result of which a new, selective reagent for cobalt is obtained.

The authors wish to thank S. S. Djohshi for his assistance and for G. B. Singh for enabling the work to be carried out.

SUMMARY

p-Nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone are suggested as specific and sensitive reagents for cobalt. A deep violet colored complex is formed with the former, while a deep red color is given by the latter reagent. Interference from nickel is supressed by addition of potassium cyanide. The limits of identification are 0.1 and 0.25 μg of cobalt respectively, while the dilution limits are 1 in 2 000 000 and 1 in 1 000 000 respectively.

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DETECTION OF BORON IN SILICATE ORES BY A TRITURATION METHOD

E. P. Ozhigov, V. S. Lozinskaya, and A. L. Krasnitskaya

Far-East Branch of the Siberian Section of the Academy of Sciences USSR, Vladivostok

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During qualitative detection of boron by combustion as volatile methyl borate [1], or in the form of its fluoride [1], compounds of copper, barium, and some other elements color the flame green [2,3]. Detection of boron with curcumin [2,4,5,6] is difficult in the presence of hydrochloric acid solutions of zirconium, titanium, and molybdenum, and also in the presence of oxidizing agents. Oxidizing agents and fluorides interfere with the use of chromotrope 2B (sodium p-nitrobenzene-azo-2-chromotropate)[6]. Detection of boron with quinalizarin suffers from the same defects when preliminary decomposition is effected by fusion with Na_2CO_3. According to Isakov [7], oxidizing agents (nitrates, chromates, and hydrogen peroxide) and colored ions (trivalent iron, copper, cobalt, tri- and sexivalent chromium, quinquevalent vanadium, and sexi- and septivalent manganese) interfere with detection of boron by means of quinalizarin. Isakov has suggested detection of boron by triturating the ore to be tested with quinalizarin in the presence of 1-2 drops of sulfuric acid. By using this technique it was found possible to limit the effect of interfering impurities and to increase the sensitivity of detection.

The aim of the work described here was to establish the optimum conditions for carrying out this reaction, and to determine its sensitivity for complex borosilicate ores (different modifications of datolite, danburite, and axinite). The chemical composition of the ore samples tested are given in Table 1.

TABLE 1

Rock	Chemical composition, %									
	B_2O_3	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	MnO	loss on calcining	total
Varieties of datolite										
a) Quartz-carbonate	15,90	37,35	None	2,23	1,31	34,4	0,20	0,66	7,48	99,33
b) Garnet	8,93	37,18	0,19	1,08	13,71	34,7	0,39	0,44	3,18	99,80
c) Hedenbergite	8,77	43,32	None	8,05	None	29,20	5,51	1,70	3,35	99,90
d) Hedenbergite-garnet	9,60	40,87	1,92	4,35	6,15	31,00	2,44	0,85	3,60	100,76
Magnetic iron ore	0,14	7,63	2,40	23.79	64,20	0,65	0,22	0.25	None	99,28
Danburite	26,30	26,30	0,30	None	0,40	22,85	0,28	None	0,04	99,97
Axinite	5,72	41,27	18,70	2,90	1,18	21,68	0,26	8,10	0,51	100,32

The experimental technique consisted in the following: An aliquot of ore (40-8 mg) was triturated, first without quinalizarin in order to give the greatest reaction surface, and then with quinalizarin, the total trituration taking not more than 30 sec. One drop of concentrated sulfuric acid was added to the mixture. When the B_2O_3 content of the aliquot is 6 mg or more, the reaction goes in the cold; the ground mixture acquires a cornflower blue color. When an aliquot containing less than 6 mg of B_2O_3 is ground for a longer period, the color only appears after heating the ground mixture (until sulfur trioxide is evolved). All the samples tested gave a positive reaction for boron. The exception was the magnetic iron ore with a B_2O_3 content of 0.14%. The qualitative reaction for this material gave a noncharacteristic color, presumably because of formation of basic salts of trivalent and divalent iron with a brown color which mask and sorb the colored quinalizarin complex.

The color intensity depends on the boron content of the samples. For B_2O_3 contents greater than 8%, the color

TABLE 2

B_2O_3 concentration	B_2O_3 content of the test samples					Color after trituration
	datolite, quartz arbonate	datolite, garnet	datolite, hedenbergite	datolite, hedenbergite garnet	danburite	
Above ten percent, mg	15,90	—	—	—	26,30**	Cornflower blue
	4,8	—	—	—	0,52	
Between one and ten percent, mg	1,59*	8,93	8,77	9,60	1,80*	» »
	0,03	0,18	0,18	0,19	0,026	
Tenths of a percent, mg	0,8*, 0,4*, 0,2*	0,45*, 0,23*	0,44*, 0,22*	0,48*, 0,24*	0,9*, 0,45*, 0,22*	» »
	0,016; 0,008; 0,004	0,009 0,004	0,009 0,004	0,01, 0,005	0,013; 0,006; 0,003	
Hundredths of a percent, mg	0,1*	0,12*	0,11*	0,12*	0,11*	Violet
	0,002	0,002	0,002	0,0025	0,0015	

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*The B_2O_3 content was lowered by mixing the ore with silica sand.

**B_2O_3 was determined in danburite without heating. The color of the reaction product was dark-cornflower blue.

TABLE 3

Test material	B_2O_3 content, %	Detection of boron with quinalizarin after:	
		Fusion with Na_2CO_3	Trituration
Hedenbergite	0.5	Not detd.	Detected
Wallastannite	1.10	" "	Ditto
Dark colored ore	0.67	" "	"
Lime with hedenbergite inclusions	0.18	" "	"
Silica schist	None	" "	Not detected

of the reaction products after trituration is dark blue; at lower B_2O_3 contents the color intensity is weaker.

In order to establish the reaction sensitivity, samples containing boron were mixed with ground amorphous silica, and powders were prepared in tnis way which contained very small amounts of B_2O_3. All these powders after trituration with quinalizarin and being treated with one drop of sulfuric acid gave positive reactions for boron after heating (they gave the cornflower blue color); they included mixtures containing down to 0.003 mg B_2O_3. Mixtures containing 0.002 mg B_2O_3 did not give the reaction. Results of experiments carried out to establish the sensitivity are given in Table 2. As these results show, the limit of identification is 3 μg of B_2O_3.

The sensitivity of the qualitative reaction for boron by the quinalizarin trituration method was tested out on various rocks and minerals after preliminary decomposition of the ore by fusion with Na_2CO_3. Silicate rock was fused on the lid of a platinum crucible with a small amount of Na_2CO_3 [1]. The melt was leached with water and the extract evaporated to dryness. A solution of quinalizarin in sulfuric acid was added to the residue and the mixture heated gently. When no interfering impurities were present, the violet color of the quanlizarin changed to blue in the presence of boron.

Comparative results are given in Table 3.

As the results in Table 3 show, after fusion with Na_2CO_3, boron could not be detected in the samples by means of quinalizarin, since the melts and their extracts had a dark-green color, which testified to the presence of large amounts of manganese in the samples.

It should be pointed out that after prolonged trituration (for more than one minute) the blue color may not even appear because of the formation of a large amount of colored reaction products which mask the color. Accordingly trituration should be not too vigorous and should be of short duration.

From the results given it is clear that the trituration method ensures higher sensitivity and reliability than the fusion method. Minerals which have varying lattice energies and lattice parameters are present in borosilicate rocks. Minerals with a low crystal lattice energy will be the first to be destroyed [8].

As an example we give below the composition and structure of minerals which accompany datolite, according to Betekhtin [9], and also the energy of their crystal lattices calculated by Fersman's method [10, 11].*

Mineral	−U, kcal/mole
Hedenbergite $CaFe[Si_2O_6]$	7593.7
Manganese-hedenbergite $CaMn[Si_2O_6]$	7563.0
Garnet	
grossularite $Ca_3Al_2[SiO_4]_3$	5992.7
andradite $Ca_3Fe_2[SiO_4]_3$	6043.9
Datolite $Ca_2B_2[SiO_4][OH]_2$	5567.5
Calcite $CaCO_3$	648

On the basis of the results on the energies of the crystal lattices of silicate minerals, it follows that hedenbergite will be the hardest to break down from silicates, and datolite the easiest. It is also obvious that these minerals will dissolve in sulfuric acid at the same relative rates. In fact, Berlin [12] has demonstrated experimentally that the rate and extent of dissolution of minerals which compose datolite ore are not the same: datolite mineral is decomposed most rapidly and completely, and decomposes to the extent of 96-100% in 60 min; garnet decomposes to the extent of 12-20% in the same period, hedenbergite decomposes to the extent of 2-4%, and calcite 47-50%. The slow rate of dissolution of calcite can be explained by formation of a sparingly soluble film of gypsum on its surface.

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* Where possible, calculations were based on the eka complex anions.

Accordingly, during trituration of datolite ore the first of the silicate minerals to be broken down and to dissolve in sulfuric acid will be the mineral datolite, so that the boric acid will dissolve, while the interfering impurities (manganese, iron) will remain in the solid phase. This is the reason for the high sensitivity of the triturating method of detecting boron in datolite ore, and for the weak interference from impurities.

It should be noted that the reactivity of various borosilicates and the sensitivity with which boron can be detected in them will also depend on the energy of the crystalline lattice.

Mineral	−U, kcal/ mole
Axinite $Ca_2[Mn, Fe]Al_2BSi_4O_{15}[OH]$	7785,4
Datolite $Ca_2B_2[SiO_4]_2[OH]_2$	5567.5
Danburite $Ca[B_2Si_2O_8]$	4930.0

Boron is detected with the greatest difficulty in the mineral axinite and is most readily detected in danburite. The limit of identification for axinite is 30 μg, for datolite 3 μg and for danburite less than 3 μg.

SUMMARY

Boron can be readily detected in borosilicate ores (in various species of datolite and in danburite) by triturating them with quinalizarin and then treating the mixture with 1-2 drops of sulfuric acid.

It has been shown that the reactivity of borosilicates and the limit of identification depend on the lattice energies of the minerals composing the ore.

The optimum conditions for detecting boron are gentle and brief trituration (not more than 30 sec) followed by heating of the reactants until sulfur trioxide fumes are evolved.

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CHROMATOGRAPHIC SEPARATION OF HALIDE IONS

G. L. Starobinets and S. A. Mechkovskii

V. I. Lenin Belorussian State University, Minsk

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Development of chromatographic methods of separating anions became possible after strongly unifunctional anion exchange resins became available [1]. Quantitative separation of fluoride, chloride, bromide, and iodide anions is a fairly difficult analytical problem; development of rational chromatographic methods of separating them is accordingly desirable [2]. Insufficient work has been carried out along these lines hitherto. Equilibrium absorption of binary mixtures of chloride-bromide ions and bromide-iodide ions by chromatographic grade alumina has been studied under static conditions [3]. Rieman and Lindenbaum [4] have separated mixtures of potassium chloride and bromide on the strongly basic anion exchange resin Amberlite XE-67 in the nitrate form. The work carried out by Attebery and Boyd is the only one in which a study was made of the chromatographic separation of mixtures of fluoride, chloride, bromide, and iodide ions; separation of a mixture of the ammonium halides on the anion exchange resin Dowex-2 in the nitrate form was, however, not completely quantitative.

We thought that the use of cation exchange resins for separating anions by partition chromatography might be a promising approach. The use of cation exchange resins for this purpose should be based on a study of the distribution of the components of an aqueous-organic mixture between the ion exchange resin phase and the solution, and also on a study of the partition coefficients of the materials being separated between both phases.

EXPERIMENTAL

Cation exchange resin SBS containing 70% styrene was prepared by sulfonating a butadiene-styrene vulcanizate containing 3 parts by weight of combined sulfur and 100 parts by weight of the copolymer with 95% sulfuric acid for 10 hr at 100°. The exchange capacity of the cation exchange resin with respect to sodium chloride proved to be 3.43 mg-equiv per g of dry ion exchange resin. The degree of swelling of the ion exchange resin in the H and in the Na forms was 2.35 and 2.05 g per g of dry resin respectively.

A study was made of the distribution of the components of aqueous-methanol and aqueous-acetone mixtures* between the cation exchange resin in the hydrogen and sodium forms and the binary solutions, throughout a whole range of compositions of the binary solutions.

First, the swelling of both forms of the resin in binary mixtures of varying composition was studied by a technique given in [6]. The swollen resin was brought to an "surface dry" state by centrifuging in a beaker with a grid bottom; an accurately weighed aliquot of the centrifuged resin was then brought to constant weight in a weighing bottle at 105°.

In order to study the distribution of the components of the binary solution, an accurately weighed aliquot of about 1 g was placed in a 25-ml bottle with a well-fitting ground glass stopper, and 15 ml of a binary solution of known composition poured into the flask; the moisture content of the ion exchange resin was taken into account in preparing the binary solution. After 24 hours the solution was replaced by 15 ml of a solution with the initial composition. This operation was repeated until the composition of the solution found in equilibrium with the ion exchange resin became equal to the original composition of the solution, which was usually expressed by a round number for the molar fraction of the nonaqueous component.

In order to determine the composition of the binary solution in the resin phase, the latter was brought to a surface dry state by centrifuging, and part of this resin was transferred to a tared bottle containing 40 ml of water. The increase in weight of the bottle is equal to the weight of swollen resin, and since the degree of swelling as a function of the composition of the quilibrium solution has already been studied, the weight of dry resin introduced into the bottle was also known.

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* Absolute methanol and acetone were prepared according to [5].

It was established experimentally that the nonaqueous component is quantitatively extracted from the ion exchange resin phase in one extraction. The concentration of this component was determined on a liquid interferometer using a calibration curve constructed beforehand.

The difference between total swelling and content of nonaqueous component is equal to the water content of the aliquot of resin taken. The composition of the solution in the resin phase was expressed as molar fractions of the nonaqueous component. The results obtained N_2I are plotted as a function of the molar fraction of the nonaqueous component in the equilibrium binary solution N_2; four of the systems studied are shown in Fig. 1.

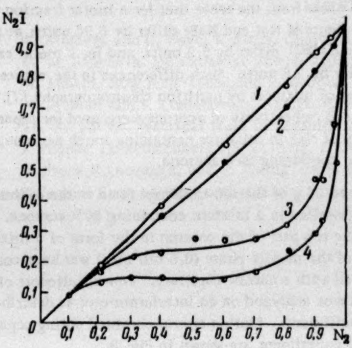

Fig. 1. Molar fraction of nonaqueous component in the resin phase (N_2I) as a function of the molar fraction of this component in the solution phase (N_2). 1) Water-methanol-resin in the H form; 2) water-methanol-resin in the Na form; 3) water-acetone-resin in the H form; 4) water-acetone-resin in the Na form.

The figure clearly shows that the components of the aqueous-methanolic mixtures are distributed almost uniformly between the resin phase and the binary solution phase. This is especially the case for the resin in the hydrogen form, for which the partition curve of the components almost fuses with the diagonal of the $N_2I - N_2$ square. Aqueous-acetone mixtures are distributed unevenly between both phases. Asymmetry is particularly clearly marked for the resin in the sodium form (Curve 4). It is clear from Fig. 1 that the Na ion exchange resin phase which is in equilibrium with the solution, and whose molar fraction of acetone is 0.7, contains 82 mole percent of water. This fact means that it should be possible to realize efficient partition chromatography on the carrier—the ion exchange resin in the sodium form containing the aqueous-acetone mixture with a predominating water content as the stationary phase, and a mobile phase in which acetone predominates.

In order to study the partition of sodium halides between the phases, analytical grade reagents which were not subjected to further purification were used. To flasks containing an aliquot of air-dry resin corresponding to 2 g of the dry resin was added acetone and water in such amounts that after taking into account the water content of the resin and its degree of swelling with respect to water and acetone, 15 ml of a solution of a given composition was obtained. Varying amounts of sodium halide corresponding to variations in salt concentration over the range 0.05 to 1.0 mg/ml were then added to these flasks. Experiments were carried out at 22° for 24 hr with periodic shaking. Special experiments established that this period was in excess of that required to establish equilibrium distribution of the salts between both phases. Next, 10 ml of the equilibrium solution was evaporated on a water bath at 100°; the dry residue was dissolved in 10 ml of distilled water and the salt concentration of the solution obtained determined on an interferometer using calibration curves which were constructed beforehand for all the halides. The salt content of the resin phase was determined by the difference between its content in the original and equilibrium solutions. On the basis of the results obtained, a partition isotherm was constructed within the coordinates salt concentration in the resin phase vs. salt concentration in the equilibrium solution. The concentration was expressed in both phases as mg/ml[*] Over the halide concentration range studied the partition lines are completely linear, as is evident, e.g., from Fig. 2 in which are shown the partition isotherms for solutions of NaCl and NaBr for a molar fraction of 0.7 of acetone in the external solution.

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[*] The volume of the solution in the swollen resin phase was calculated on the basis of data on the densities of aqueous-acetone mixtures [8].

Partition Coefficients

Salt	Solubility, g/100 ml water	N_2	K	Salt	Solubility, g/100 ml water	N_2	K
NaI	178,7	0,8	2,05	NaCl	36,0	0,7	7,90
NaBr	90,5	0,8	9,0	NaCl	36,0	0,5	3,45
NaBr	90,5	0,7	2,65	NaF	4,2	0,5	11,1

A summary of the results obtained for the partition coefficients are given in the table; they are equal to the slopes of the partition isotherms.

The table shows that the salt which is most soluble in water (NaI) has the lowest partition coefficient, and vice versa. This is explained by the fact that the lower the solubility of a salt, the more strongly pronounced is the decrease in solubility produced by addition of acetone. It is also clear from the table that for a molar fraction of acetone in the equilibrium solution of 0.8, the partition coefficients of NaI and NaBr differ by 6.95 units; at a molar ratio of 0.7 for acetone the partition coefficients of NaBr and NaCl differ by 5.2 units, and for a molar ratio of 0.5 for acetone the partition coefficients of NaCl and NaF differ by 7.6 units. Such differences in the values of the partition coefficients are quite sufficient for a clear separation of mixtures by partition chromatography [7]. Accordingly, mobile phases with molar fractions of 0.8, 0.7, and 0.5 respectively of acetone were used for separating NaI, NaBr, and NaCl. Bearing in mind the very low solubility of NaF in mixtures containing much acetone, in order to compress its zone this material was eluted with a mixture containing 30% acetone.

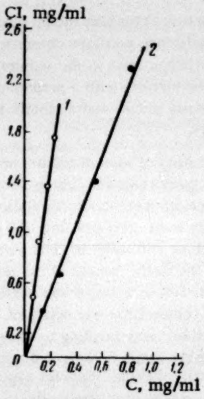

Fig. 2. Partition isotherms. 1) NaCl and 2) NaBr at a molar ratio of 0.7 of acetone.

A 50 × 2 cm column contained 32 g of the ion exchange resin in the sodium form (particle size 0.25-0.50 mm) swollen in a mixture containing 80% acetone. The halides were introduced into the top part of the column in the form of a mixture of the solid salts. The throughput of the mobile phase (0.5 ml/min) was kept constant by means of a Mariott flask provided with a narrow capillary. Ten-ml aliquots of eluate were collected and each aliquot analyzed on an interformmeter as described during the study of the partition coefficients. Elution curves obtained during separation of the four halides in a typical experiment are shown in Fig. 3.

15.0 mg NaI, 20.2 mg NaBr, 15.0 mg NaCl, and 20.0 mg NaF were introduced into the column. On the basis of the areas under the peaks on the elution curves, the values obtained for the respective salts were 14.9, 19.8, 15.0 and 20.2 mg. Thus separation is strictly quantitative, the error not being greater than 1%. Not only do the zones not overlap each other (as observed previously [1]) but there are clear gaps between the zones, the value of which is determined by the time taken to replace one mobile solvent by the next. The elution curves are arranged in order of increasing partition coefficient, no tailing is observed, and the curves are almost ideal Gaussian error curves. It follows therefore that our experiments are covered by the theory of partition chromatography, and are not complicated by side effects.

By varying the degree of cross-linking of the resin, and also the nature and composition of the binary solutions, it is possible to change the partition coefficients of the materials to be separated very accurately and over extremely wide limits. The

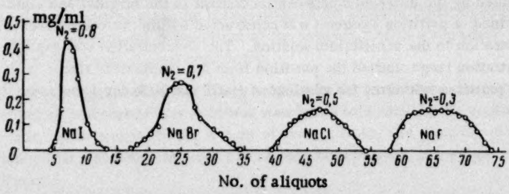

Fig. 3. Elution curves of Na halides. N_2 is the molar fraction of acetone in the mobile phase.

method outlined here therefore can be widely applied to the development of chromatographic methods of separating complex mixtures of anions.

SUMMARY

A study has been made of the partition of the components of aqueous-methanol and aqueous-acetone mixtures between the cation exchange resin SBS in its hydrogen and sodium forms and the binary solutions, over a whole range of varying compositions of the binary solutions.

The partition coefficients of sodium halides between the resin in its sodium form and aqueous-acetone mixtures have been studied.

On the basis of the results obtained a method has been developed for the quantitative chromatographic separation of mixtures of sodium halides.

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SIMULTANEOUS DETERMINATION OF HYPOCHLORITES, CHLORITES, AN CHEORATES BY MEANS OF ARSENITE, USING OsO_4 AS CATALYT

P. K. Norkus and A. Yu. Prokopchik
Institute of Chemistry and Chemical Technology, Academy of Sciences,
Lithuanian SSR, Vilnius

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Little work has been carried out on the titrimetric determination of oxygen compounds of chlorine in each other's presence; a review of this work is given in [1]. Almost all these methods are based on stepwise titration by means of various solutions of separate aliquots of one or more components, depending on the conditions. In the present article the possibility is demonstrated of carrying out a titrimetric determination of hypochlorites, chlorites, and chlorates by means of arsenite on one aliquot.

The hypochlorite solutions were prepared by neutralizing excess of an alkali solution of hypochlorous acid, obtained from Cl_2O formed by the interaction of yellow mercury oxide with chlorine in CCl_4 [2]. Chlorite solutions were prepared by the interaction of ClO_2 solutions, obtained from potassium chlorate, oxalic and sulfuric acids [3], with excess alkali in the presence of hydrogen peroxide [4]. A bicarbonate solution of sodium arsenite was used for titration.

An A4-M2 tube voltmeter was used for the potentiometric titration of hypochlorites and chlorites. The indicator electrode was a smooth platinum disc, while the reference electrode was a saturated calomel electrode with an agar-agar bridge filled with saturated potassium chloride solution. The solution being titrated was stirred with a magnetic stirrer. The end point was determined on the basis of the maximum value of $\Delta E/\Delta C$.

Control analyses were carried out by other methods: hypochlorite, chlorite or their total amount was determined iodometrically [5], while chlorate was determined bromatometrically [6].

a) Determination of Chlorites by Means of Arsenite. Chlorites are very slowly reduced by arsenite in alkaline media [1,7]. We have found that this process can be speeded up considerably in the presence of OsO_4. Characteristically, osmic acid is a good catalyst of many oxidation-reduction reactions [8-10], and, moreover, is used during the titrimetric determination of chlorates [11-13].

We attempted to develop a potentiometric method for determining chlorites with arsenite in the presence of OsO_4. As preliminary experiments showed, such a method is possible, the accuracy and speed of titration of chlorites being dependent on a number of factors.

Since chlorite solutions as a rule contain some chlorates, determination of chlorites must be carried out in an alkaline medium, since in acid solutions in the presence of OsO_4 reduction of chlorates is possible [8-13]. It was established that when the chlorite solution to be titrated was made alkaline with sodium hydroxide, normally only hot solutions are titrated. Moreover, when solutions are made alkaline, it is impossible to titrate even hot solutions of the chlorites of the alkaline earth metal (in particular the chlorites of strontium and barium); this is most probably the result of catalyst deactivation.

Titration is significantly improved and simplified by using sodium carbonate for rendering the test solution alkaline. A characteristic feature in this case is that the reaction between arsenite and chlorite in the presence of OsO_4 proceeds appreciably more rapidly, and titrimetric determination of chlorite becomes possible even at room temperature. By using Na_2CO_3 for alkalinification it is also possible to titrate the alkaline earth metal chlorites. In this case sodium carbonate precipitates the alkaline earth metals as their carbonates, the presence of the precipitates of which does not affect the catalyst activity.

Too large an excess of catalyst concentration must be avoided, since under such conditions the catalyst is itself reduced, and this inevitably affects the accuracy of chlorite determination. Accordingly, we used only 0.2 ml

TABLE 1. Determination of Chlorites Iodometrically and by the Arsenite Method

Expt. No.	Chlorite	Chlorite determined, meq		Deviation, %	Acid to the original solution	
		iodometrically	by the potentiometric arsenite method		1 M Na_2CO_3, ml	chlorate, meq
1	Sodium	1,793	1,793	0	2	—
2		1,793	1,793	0	10	—
3		1,793	1,791	—0,11	5	2,2
4		1,793	1,798	+0,27	3	13,2
5		1,793	1,790	—0,17	3	8,8
6		3,586	3,590	+0,11	4	—
7	Calcium	2,163	2,162	—0,05	2	—
8		2,163	2,161	—0,09	10	—
9		2,164	2,163	0	5	4,4
10	Strontium	2,147	2,149	+0,09	3	—
11		2,147	2,150	+0,14	10	—
12		2,147	2,148	+0,05	5	8,8
13	Barium	2,145	2,147	+0,09	5	—
14		2,145	2,145	0	5	11,0

(4-5 drops) of a 0,1% solution of OsO_4 for each determination. This negligibly small amount of catalyst has almost no effect on the accuracy of a determination; it is sufficient, however, to speed up the reaction.

Table 1 contains results for titration of chlorites (10-20 ml) obtained with the new method of titrating with 0,1 N arsenite solution in the presence of OsO_4; these results are compared with those obtained by the usual iodometric method [5].

As the results in Table 1 show, chlorites can be titrated fairly accurately. It should be pointed out that when the test solution is made alkaline with sodium carbonate, neither the accuracy nor the speed of potentiometric titration drop even when a large excess of carbonate is used. The presence of even large amounts of chlorate has almost no effect on the accuracy of chlorite determination (see Table 3).

TABLE 2. Determination of Hypochlorites by the Iodometric and Arsenite Methods

Expt. No.	Hypochlorite	Hypochlorite determined		Deviation, %	Added to the original solution		
		iodometrically	by the potentiometric arsenite method		1 M Na_2CO_3, ml	1 N NaOH, ml	chlorite, meq
1	Sodium	1,252	1,250	—0,16	5	—	—
2		1,252	~1,36	>+8	5	—	8,97
3		1,252	1,254	+0,16	—	3	2,99
4		1,252	1,250	—0,16	—	10	8,97
5		1,252	*	—	—	3	8,97
6	Calcium	1,828	1,828	0	—	—	—
7		1,828	1,833	+0,28	5	—	—
8		1,828	1,828	0	—	10	10,82
9		1,828	*	—	—	3	10,82
10	Strontium	1,185	1,184	—0,09	—	—	—
11		1,185	1,184	—0,09	—	10	—
12		1,185	1,185	0	—	5	10,74
13		1,185	*	—	—	2	10,74
14	Barium	1,638	1,639	+0,06	—	—	—
15		1,638	1,638	0	5	—	—
16		1,638	~1,74	>+6	5	—	2,84
17		1,638	1,636	—0,12	—	5	—
18		1,638	1,638	0	—	3	2,14
19		1,638	1,638	0	—	10	12,84
20		1,638	*	—	—	3	12,84

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* Solutions yellowed during titration (ClO_2 evolved); the end point could not be determined.

b) Determination of Hypochlorites by Means of Arsenite. In the given instance the most suitable method would appear to be a potentiometric determination of hypochlorites in an alkaline medium (pH > 9) by the method of Flis and Bynyaeva [7]. Their paper, however, does not contain any actual data on the amount of chlorite present, and there is no mention of titration of alkaline earth metal hypochlorites. Accordingly, we carried out several additional potentiometric determinations of hypochlorites in which the effects of alkalinification and the presence of chlorate in the test solutions were examined. The experimental results obtained during titration of hypochlorites (10-20 ml) with 0.1 N arsenite solution are given in Table 2; these results are compared with those obtained by the cited iodometric method.

As the results in Table 2 show, during titration of hypochlorites with arsenite some characteristic features are observed.

Firstly, titration of hypochlorite in the absence of chlorite can be carried out whatever method is used for alkalinification. When, however, chlorite is present, alkalinification of test solution with sodium carbonate leads to sharp increase in the results for hypochlorite (Table 2, expts. 2 and 16). We think that this can be explained by the fact that the carbonate medium favors interaction of arsenite with chlorite.

Secondly, and this is the most important feature, with increasing chlorite concentration in the test solution, the solution must be made more alkaline with sodium hydroxide. As is evident from the results given in Table 2 (expts. 5,9,13,10) when the original alkalinity of the test solution is too low, potentiometric determination of hypochlorites in the presence of chlorites becomes impossible. When the solution is not alkaline enough, during titration with arsenite, chlorine dioxide starts to come off, and this colors the solution yellow; moreover, the pH of such solutions drops to 9 and lower.

c) Determination of Chlorates. For chlorate determination, we chose a bromatometric method based on titration with potassium bromate of the excess arsenite which has not reacted with chlorate [6]. This method, however, requires a solution in which the acidity is high (1 ml of concentrated HCl per 7 ml of solution), and prolonged boiling (15 min). These drawbacks are eliminated when OsO_4 is used [11].

As our experiments showed, when the test solution contains 0.2 ml of 0.1% OsO_4 solution, it is sufficient to acidity the test solution with 1-2 ml of concentrated HCl and to boil it for only 1-2 min.

d) Simultaneous Determination of Hypochlorite, Chlorite, and Chlorate. On the basis of our results given above and on published data, we concluded that by modifying the conditions it should be possible to determine hypochlorite, chlorite, and chlorate in one aliquot by meand of arsenite. Table 3 contains some experimental results characterizing such a determination of hypochlorite, chlorite, and chlorate in each other's presence when the method given below was used.

TABLE 3. Determination of Hypochlorites, Chlorites, and Chlorates in Mixtures

Expt. No.	Salt mixture	Determined, meq			Total in meq of hypochlorite and chlorite	
		hypochlorite	chlorite	chlorate	iodometrically	potentiometrically
1	Sodium	0,836	2,006	0,686	2,842	2,844
2		0,768	1,940	6,963	2,717	2,708
3		1,141	1,563	1,392	2,701	2,704
4		1,105	0,855	0,084	1,957	1,960
5		0,590	1,438	0,044	2,028	2,028
6	Calcium	1,098	0,840	0,064	1,942	1,938
7		2,230	1,761	0,111	3,991	3,991
8		0,716	1,220	0,859	1,931	1,936
9	Strontium	0,645	1,942	10,253	2,590	2.587
10		0,404	2,798	2,157	3,200	3,202
11	Barium	0,480	1,455	0,517	1,938	1,935
12		0,893	0,913	0,094	1,808	1,806

Determination of Hypochlorite. A known volume (10-20 ml) of test solution is alkalinified with 2-5 ml of 1 N sodium hydroxide solution. The platinum and calomel electrodes are immersed in the solution and the galvanic cell and tube voltmeter switched on. The test solution is stirred with a magnetic stirrer and titrated with arsenite solution, the potential changes being followed. Should the solution start to acquire a yellow color during titration, this may mean that the chlorite concentration is too high; determination should therefore be repeated after adding a larger amount of alkali (e.g., 10 ml of 1 N NaOH).

The arsenite is added dropwise near the end point. The end point is readily established on the basis of the maximum change in potential difference on addition of successive drops of arsenite solution, i.e., on $\Delta E / \Delta C$.

Determination of Chlorite. After hypochlorite determination, to the solution is added 1 N $NaHCO_3$ solution in an amount which is 1.5-2 times the amount of sodium hydroxide used (for converting the hydroxide to carbonate) and 4-5 drops (about 0.2 ml) of 0.1% OsO_4. At this stage the difference in potentials of the cell acquires its original value. Titration with arsenite is then continued as for hypochlorite determination until the potential jump corresponds to the end point. The concentration of the amount of chlorite is calculated from the amount of arsenite which has been used.

Determination of Chlorate. After the chlorite has been determined, the electrodes are removed from the solution and the chlorate determined bromatometrically in the same solution. For this purpose excess arsenite is added to the solution; the solution is neutralized to the methyl orange end point and then acidified with 1-2 ml of concentrated hydrochloric acid; about 0.1 g of KBr is finally added and the liquid boiled for 1-2 min. The excess arsenite is back titrated in the hot solution with bromate using methyl orange as indicator. The amount of chlorate is calculated on the basis of the difference between the amounts of original and residual arsenite.

SUMMARY

It has been established that OsO_4 catalyzes the reaction of chlorites with arsenite in an alkaline medium.

A new method has been developed for the potentiometric determination of chlorites in an alkaline medium by means of arsenite in the presence of OsO_4 as catalyst.

A new arsenitometric method is suggested for the successive determination of hypochlorites, chlorites, and chlorates in one aliquot.

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CONDITIONS FOR THE PHOTOMETRIC DETERMINATION OF FLUORIDE WITH ARSENAZO

A. F. Kuteinikov

All-Union Scientific Research Institute of Mineral Raw Material, Moscow

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The basis of all photometric methods of determining fluoride is the process of complexing the cations of metals which have been complexed beforehand by some other reagent as a colored compound into colorless fluoride compounds. During this process the color intensity of the solution decreases. Other anions which form colorless complexes with the central ions of the metals can show similar behavior. The mechanism of the formation of colored complexes and their stability has not been studied sufficiently. Many authors have pointed out the significant influence of the acidity of the solutions and of certain ions on the sensitivity and accuracy of the results [1-4]; accordingly, it is recommended that standard experimental conditions must be strictly adhered to during fluorine determination.

The most suitable reagents for fluoride determination are those which form simple complexes over a wide pH range with metals. In the present article it is suggested that solutions of certain complexes of the reagent arsenazo can be used for determining fluoride; this reagent has been suggested by Kuznetsov [5] for the determination of small amounts of rare elements. The complex of arsenazo with thorium has already found application for the determination of fluoride [6]. Many arsenazo complexes posses an intense color, changes in which can be used for fluoride determination [7].

The complexes have a simple composition (the ratio of metal to reagent in them is 1:1 or 1:2) and exist over a wide pH range, so that they can also be used for altering the sensitivity of fluoride determination over a wide concentration range.

On adding fluorides to solutions of the colored complexes of arsenazo, some of the metal is complexed into a colorless fluoride complex, while part of the reagent changes to the free state. The optical density of solutions decreases at wave lengths characteristic of the complexes, and increases at wave lengths characteristic of the reagent. In Fig. 1 are shown as examples the change in the absorption spectra of solutions of the complex compounds of arsenazo with the uranyl ion on adding sodium fluoride to them at varying pH's. Fig. 2 shows the changes in the concentration of the colored complex under the action of fluoride at various acidities of the solutions.

Calibration curves for the determination of fluorine are shown in Fig. 3. Calibration curves were constructed as follows. One-ml lots of $5 \cdot 10^{-4}$ M uranium in the form of an aqueous uranyl nitrate solution, and 1-ml lots of $8.5 \cdot 10^{-4}$ M aqueous arsenazo solution, were introduced into a series of 25-ml standard flasks; 2 ml of a 0.5 N solution of an acetate buffer mixture was then added to each flask to establish the requisite pH. Fluorine was added to the solutions in the flasks in the form of sodium fluoride solution. All the solutions were made up to the mark with water and carefully mixed; after standing for 15-20 min their optical density was measured at 620 mμ in a 10-mm cuvette. The sensitivity of the determination depends on the conditions under which the reaction is carried out (Fig. 3). Accordingly, by varying them it is possible to determine fluoride over a wide concentration range: from hundredths of a microgram to milligrams per ml.

The optical density of solutions of the complexes of zirconium, thorium, and aluminum with arsenazo was determined in the same way on adding varying amounts of fluoride.

Table 1 contains the conditions for fluoride determination and the sensitivity of the method on using arsenazo with various metals (cuvette with a transmission layer of 10 mm). Optical density was measured on an SF-4 spectrophotometer. From the results given in Figs. 1-3 and in Table 1, it is clear that the effect of fluoride ions decreases with increasing pH. This is explained by the fact that the reagent arsenazo is a sexibasic acid, the last four dissociation stages of which characterize arsenazo as a weak acid [8].

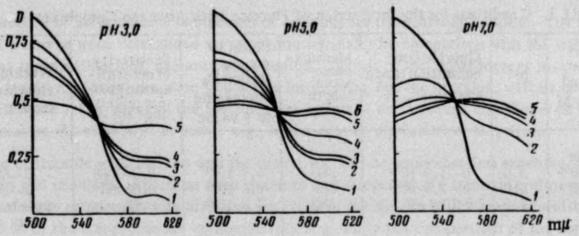

Fig. 1. Changes in the absorption spectra of solutions of the uranyl-arsenazo complex on adding sodium fluoride. Uranium concentration $2 \cdot 10^{-5}$ M; arsenazo concentration $3.4 \cdot 10^{-5}$ M. Series of curves at pH 3.0: 1) fluoride concentration $1 \cdot 10^{-3}$ M; 2) $4 \cdot 10^{-4}$ M; 3) $2 \cdot 10^{-4}$; 4) 10^{-4}; 5) 0.0. Series of curves at pH 5.0: 1) fluoride concentration $1 \cdot 10^{-2}$ M; 2) $6 \cdot 10^{-3}$; 3) $4 \cdot 10^{-3}$; 4) $2 \cdot 10^{-3}$; 5) $1 \cdot 10^{-3}$; 6) 0.0. Series of curves at pH 7.5: 1) fluoride concentration $3.5 \cdot 10^{-1}$; 2) $2 \cdot 10^{-1}$; 3) $1 \cdot 10^{-1}$; 4) 0.0; 5) $5 \cdot 10^{-1}$.

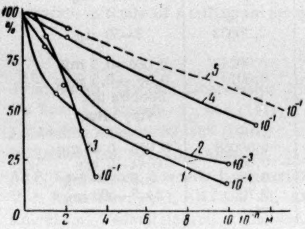

Fig. 2. Change in the concentration of the uranyl-arsenazo complex on adding fluoride. Uranium concentration $2 \cdot 10^{-5}$ M, arsenazo concentration $3.4 \cdot 10^{-5}$ M. 1) pH 3.0; 2) pH 5.0; 3) pH 7.5; 4) pH 9.0; 5) pH 10.0.

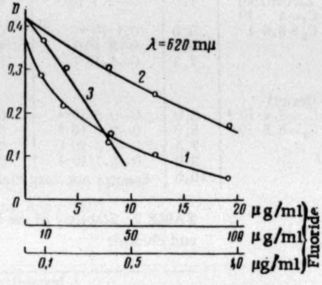

Fig. 3. Calibration curve for fluoride determination on the basis of the decrease in the color intensity of the uranyl-arsenazo complex. Uranium concentration $2.0 \cdot 10^{-5}$ M; reagent concentration $3.4 \cdot 10^{-5}$M. 1) pH 3.0; 2) 5.0; 3) 7.0.

As shown earlier [9], metal ions replace the hydrogen ions in the arseno group or in the hydroxy group of the arseno molecule, splitting of hydrogen from which is exactly characterized by low values of the dissociation constants. Accordingly, on increasing the pH the concentration of the coordinated anions of the reagent increases, and consequently the resistance to the destructive action of fluoride ions on the color increases. On the other hand, on lowering the pH the destructive effect of fluoride on the color increases, and in certain cases can give rise to conditions such that the effective stability of the fluoride complex will he higher than the effective stability of the colored complex (e.g., in the system aluminum-arsenazo-fluoride at pH 3.5-4.5).

Under these conditions the fluoride is complexed with the metal into a complex in equivalent amounts; consequently, similar conditions can be used for the titrimetric determination of fluorine. The regularities indicated are confirmed experimentally by the results of the present work.

The results in Table 1 show that determination of fluoride on the basis of the extinction of the color of the arsenazo complex with aluminum is more sensitive than when other ions are used to form complexes with arsenazo; the color of the aluminum complex, however, depends to a greater extent on pH. The relatively high sensitivity of

TABLE 1. Conditions for the Interaction of Fluorine with Arsenazo Complexes

Concentrations: element C_1 and reagent C_2, M	pH	Fluoride concentration range examined, M	Measurement wave length D, mμ	Fluoride concentration D_0 decreasing to ½ value	Sensitivity of determination (1.0-cm cuvette) mg/ml	Working rate of fluoride concentration (25 ml)
Aluminum						
$C_1=5,3\cdot10^{-5}$	3,0	$0-1,9\cdot10^{-4}$	580	$5,4\cdot10^{-5}$	0,000068	2—50 μg
$C_2=6,8\cdot10^{-5}$	5,0	$0-2,9\cdot10^{-4}$	580	$6,5\cdot10^{-5}$	0,00003	2—50 μg
	7,5	$2,9\cdot10^{-3}-2\cdot10^{-2}$	580	$1,2\cdot10^{-2}$	0,12	Spectra not very clear
$C_1=4\cdot10^{-5}$ $C_2=8\cdot10^{-5}$	4,5	$0-8,3\cdot10^{-5}$	575	$3,4\cdot10^{-5}$	0,000026	2—40 μg
$C_1=8\cdot10^{-5}$ $C_2=8\cdot10^{-5}$	4,5	$0-1,7\cdot10^{-4}$	575	$7,6\cdot10^{-5}$	0,000037	2—70 μg
Thorium	1,4	$0-4,2\cdot10^{-4}$	600	$1,3\cdot10^{-4}$	0,00007	5—100μg
$C_1=4\cdot10^{-5}$	2,05	$0-4,2\cdot10^{-4}$	600	$2,3\cdot10^{-4}$	0,00014	0,01—0,2mg
$C_2=6\cdot10^{-5}$	2,95	$0-4,2\cdot10^{-4}$	600	$2,7\cdot10^{-4}$	0,00014	0,01—0,2mg
	2,7	$0-2,1\cdot10^{-3}$	600	$8,7\cdot10^{-4}$	0,00055	0,01—1 mg
	5,3	$0-3,1\cdot10^{-3}$	600	$1,3\cdot10^{-3}$	0,00073	0,02—1,5mg
	5,8	$0-4,2\cdot10^{-3}$	600	$2,3\cdot10^{-3}$	0,0013	0,035—2,0mg
	7,0	$0-2,1\cdot10^{-2}$	600	$6,7\cdot10^{-3}$	0,0059	0,15—10 mg
	9,0	$0-2.1\cdot10^{-1}$	600	$1,1\cdot10^{-1}$	0,080	2,0—50 mg
	10,5	Spectra not very clear				
Zirconium	1,0	$0-2,4\cdot10^{-4}$	620	$7\cdot10^{-5}$	0,00032	8—50 μg
$C_1=4\ \cdot10$ $C_2=3,4\cdot1$	3,0	$0,1\cdot10^{-3}$	620	$3,5\cdot10^{-4}$	0,0024	0,060—0,5 mg
	5,0	$0-8\cdot10^{-3}$	620	$6\cdot10^{-4}$	0,0019	0,05 —0,5 mg
	7,5	$0-1\cdot10^{-1}$	620	$1\cdot10^{-1}$	0,95	Spectra not very clear
Uranyl						
$C_1=3,4\cdot10^{-5}$	3,0	$0-9,6\cdot10^{-4}$	620	$2,5\cdot10^{-4}$	0,00058	0,015—0,45 mg
$C_2=6,8\cdot10^{-5}$	5,0	$0-9,6\cdot10^{-3}$	620	$4\cdot10^{-3}$	0,0057	0,14—5 mg
	7,5	$0-3,4\cdot10^{-1}$	620	$2,5\cdot10^{-1}$	0,19	0,5—100 mg
	9,0	$0-5,7\cdot10^{-1}$	620	1,1	0,72	14,5—500 mg
	10,5	Spectra not very clear				

TABLE 2. Stability of the Complex Compounds of Arsenazo and Fluoride

Element	Instability constants of the complexes		Ratio of instability constants $K_a : K_F$
	with arsenazo	with fluoride	
Aluminum	$1,5\cdot10^{-10}$	$4,8\cdot10^{-7}$	$3\cdot10^{-4}$
Beryllium	$2,2\cdot10^{-9}$	$1,4\cdot10^{-6}$	$1,57\cdot10^{-3}$
Gallium	$1,7\cdot10^{-10}$	—	—
Iron	$3,9\cdot10^{-14}$	$1,9\cdot10^{-6}$	$2\cdot10^{-8}$
Indium	$1,9\cdot10^{-11}$	—	—
Rare earths	$1,0\cdot10^{-10}$	$1\cdot10^{-4}$	$1\cdot10^{-6}$
Thorium	$1,6\cdot10^{-16}$	$1,6\cdot10^{-8}$	$1\cdot10^{-8}$
Titanium	$5,8\cdot10^{-18}$	$1\cdot10^{-7}$	$6,0\cdot10^{-10}$
Uranium (IV)	$6,0\cdot10^{-17}$	10^{-7}	$6\cdot10^{-6}$
Uranyl ion	$2,5\cdot10^{-12}$	10^{-6}	$2,5\cdot10^{-6}$
Zirconium	$1,9\cdot10^{-17}$	$1,15\cdot10^{-9}$	$1,65\cdot10^{-8}$

fluoride determination with aluminum is related to the lower stability of the complex formed between aluminum and arsenazo compared with the stabilities of the remaining complexes. A buffer solution must be used to standardize the experimental conditions and the reproducibility of the results. The amount of buffer solution added should be constant in all series of experiments, since the acetate ion which enters into its composition also forms a fairly stable complex with aluminum cations and uranyl ions.

Table 2 contains some properties of the complex compounds of arsenazo and fluoride, which make it possible to evaluate the possibility of using colored compounds of arsenazo for determining fluoride. The K_{instab} values of the complexes of arsenazo were determined spectrophotometrically by comparison with the stability of the colorless complexes of the metals (fluorides, oxalates, etc.) studied. Details of the experimental method used are given in [9]. The highest sensitivity, using the same conditions for carrying out the reaction, will be observed in those cases where the difference in the value of the instability constants of the arsenazo complexes on the one hand, and the fluoride complexes on the other, will be least, e.g., in the case of aluminum or beryllium.

Determination of fluoride with thorium and the uranyl ion will be somewhat less sensitive, and even less sensitive with zirconium and titanium. Reactions with titanium and zirconium are insuitable also, since the absorption spectra of solutions of their compounds with arsenazo are close to the spectra of the reagent and the molar extinction coefficient of solutions of the complexes are comparatively low, while the composition of the complexes changes with pH. In addition, the reactions of zirconium and quadrivalent titanium are unbalanced; the ions hydrolyze, as a result of which nonreproducible results are obtained. This last fact shoud be borne in mind in other methods where colored titanium and zirconium complexes are used.

SUMMARY

Colored complexes of the reagent arsenazo have been used for the determination of fluoride ions. The most suitable compounds for this purpose are those of aluminum, the uranyl ion, beryllium, thorium, and the rare earths.

Conditions are given for the determination of fluoride ions over a wide concentration range (from hundredths of a microgram to tenths of a milligram per ml) on the basis of the decrease in color intensity.

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SEPARATE POTENTIOMETRIC TITRATION OF MIXTURES OF ORGANIC BASES IN A METHYL ETHYL KETONE MEDIUM WITH PERCHLORIC ACID SOLUTION

A. P. Kreshkov, L. N. Bykova, and N. Sh. Shemet

D. I. Mendeleev Moscow Chemico-Technological Institute

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Numerous investigations in the field of solutions carried out by the Russian school of chemists under D. I. Mendeleev [1-3] have exposed the extremely important fact of the influence of the individual character of a solvent on the state of the dissolved material in solution.

It has been found that the same material, e.g., urea [4], can behave in various ways depending on the nature of the solvent. It is possible to titrate in nonaqueous solvents weak and very weak acids and bases which cannot be titrated in aqueous media because of high pK_{base} values.

Anhydrous acetic acid is the medium that is most frequently used for titrating bases [5-8]. It is possible to titrate such bases as amines, alkaloids, and antibiotics, etc., in acetic acid with reasonable accuracy [9]. As a titration medium, however, acetic acid has several disadvantages [10].

All strongly protegenic solvents have a leveling effect on base strength, so that it is impossible to determine bases separately in their mixtures. Recently, in some instances, formic acid [11], a mixture of acetic and formic acids [12], acetic acid and its anhydride [13], butyric acid [14], propionic acid [15], and other acids have started to find application for titrating weak bases instead of acetic acid.

Theoretical considerations relating to the use of protogenic solvents of the acetic acid type as titration media have been considered by Izmailov [16].

Fritz [17] has used acetonitrile as a medium for titration mixtures of bases. Since solutions of perchloric acid in acetonitrile are unstable, titration was carried out with a solution of perchloric acid in dioxane. The author succeeded in carrying out separate determination of di-n-butylamine and pyridine, aniline and o-chloroaniline, β-phenylethylamine and aniline, pyridine and caffeine, aniline and sulfothiazole. It is also possible to titrate mixtures of Schiff bases and the original amine in an acetonitrile medium [18].

Dalit has carried out separate titrations of diethylamine and pyridine in their mixtures in a propylene glycol–chloroform medium. Nevertheless, on titrating a mixture of diethylamine and aniline in the same solvent only one potential jump corresponding to the total of both bases was obtained. It has been found possible to carry out potentiometric titration of the following two-component mixtures in an ethylene glycol–phenol medium (1:1): triethylamine and aniline, triethylamine and pyridine, and ammonia and an aqueous solution of pyridine [10].

Pifer, Wollish, and Schmall [19] have titrated mixtures of potassium and ammonium acetates with n-butylamine or pyridine in an acetic acid–chloroform (1:10) medium.

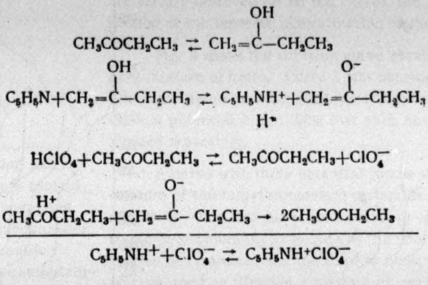
Bruss and Wyld [20] have titrated acid mixtures and also piperidine and pyridine in a methyl isobutyl ketone medium.

We have tested protogenic solvents (acetic, formic, and propionic acids), amphoteric solvents, and a series of inert solvents as media for titrating mixtures of organic bases. The use of solvents which do not exert a levelling effect on bases makes it possible to carry out separate titration of bases in their mixtures.

Ketones proved to be the best differentiating solvents. These solvents possess both weakly acid and weakly basic properties simultaneously. Of the ketones tested, including acetone, methyl ethyl ketone, methyl butyl ketone, acetophenone, and others, methyl ethyl ketone proved to be the best. In this medium it is possible to carry out separate titration of multicomponent mixtures of strong, weak, and very weak acids [21].

On the basis of the research work indicated above, we have developed a new method for the determination of weak and very weak bases in their mixtures by titration in a methyl ethyl ketone medium, using perchloric acid dissolved in the same solvent as titrant. The method suggested has many advantages over titration of bases in an anhydrous acetic acid medium.

Taking neutralization of pyridine as an example, the neutralization of a base can be expressed in the form of the following equations:



$$CH_3COCH_2CH_3 \rightleftarrows CH_2{=}\overset{OH}{\overset{|}{C}}{-}CH_2CH_3$$

$$C_5H_5N + CH_2{=}\overset{OH}{\overset{|}{C}}{-}CH_2CH_3 \rightleftarrows C_5H_5NH^+ + CH_2{=}\overset{O^-}{\overset{|}{C}}{-}CH_2CH_3$$

$$HClO_4 + CH_3COCH_2CH_3 \rightleftarrows \overset{H^+}{CH_3COCH_2CH_3} + ClO_4^-$$

$$\underline{\overset{H^+}{CH_3COCH_2CH_3} + CH_2{=}\overset{O^-}{\overset{|}{C}}{-}\ CH_2CH_3 \rightarrow 2CH_3COCH_2CH_3}$$

$$C_5H_5NH^+ + ClO_4^- \rightleftarrows C_5H_5NH^+ClO_4^-$$

According to Izmailov [5], the change in titration conditions which occurs in nonaqueous solvent medium is explained by the change in the ratio K_S/K_B, where K_S is the ionic product of the solvent, and K_B is the dissociation constant of the base. A decrease in this ratio leads to an improvement in titration conditions. Thus for formic acid, which has strongly acid properties, $K_S = 5 \cdot 10^{-7}$, while for a weak base such as urea, $K_B = 5.6 \cdot 10^{-2}$, while in water K_B for urea is $1.5 \cdot 10^{-14}$. In an aqueous medium the ratio $\frac{K_S}{K_B} = \frac{1 \cdot 10^{-14}}{1.5 \cdot 10^{-14}} \approx 1$, while in a formic acid medium $\frac{K_S}{K_B} = \frac{5 \cdot 10^{-7}}{5.6 \cdot 10^{-2}} \approx 10^{-5}$. Accordingly, in a formic acid medium, just as in a medium of other acid solvents [22], weak bases become stronger and can be titrated with reasonable accuracy.

In an acetone medium, which possesses weakly acid properties, the ratio K_S/K_B decreases insignificantly, but the ratio is still sufficient for weak bases such as aniline and its derivatives to be nitrated in a medium of actone and other ketones.

EXPERIMENTAL

We have titrated aliphatic and aromatic primary, secondary, and tertiary amines (e.g., n-butylamine, triethylamiene, triethanolamine, aniline, dimethylaniline, diethylaniline, toluidines, etc.), heterocyclic basis (pyridine, piperidine, pyrazoles, triazoles, imidazoles etc.)in methyl ethyl ketone. Methyl ethyl ketone was carefully dehydrated by standing for a long time over anhydrous potassium carbonate. Before use it was distilled and the fraction boiling between 79-80° collected. Solutions of perchloric acid in acetic acid, dioxane, acetone, and methyl ethyl ketone were tested as titrants.

A 0.1 N solution of perchloric acid in methyl ethyl ketone is recommended for the separate determination of the components of mixtures of bases. Such a standard solution is prepared by dissolving 8-9 ml of 72% perchloric acid in 1000 ml of dried methyl ethyl ketone; the solution is saturated with dry nitrogen for 5 min. The solution is standardized either against potassium hydrogen phthalate or sodium carbonate [9]. The titer of a solution of perchloric acid in methyl ethyl ketone remains constant for a month.

The use of a dioxane solution of perchloric acid did not give such good results as the use of a perchloric acid solution prepared in methyl ethyl ketone.

Experimental Procedure. The setup consists of a 10-ml buret graduated in 0.02 ml, an LP-5 potentiometer, a magnetic stirrer, a nitrogen drying system, and a titration beaker in which glass and calomel electrodes are immersed.

An accurately weighed sample of test material (0.03-0.05 g) in transferred to the titration beaker and dissolved in 20 ml of methyl ethyl ketone.

Ten ml of the 0.1 N solution of perchloric acid in methyl ethyl ketone is squeezed into the buret by means of a rubber bulb. In order to purify and dry the air squeezed into the buret, a system of columns packed with soda lime and fused calcium chloride is inserted between the buret and the rubber bulb.

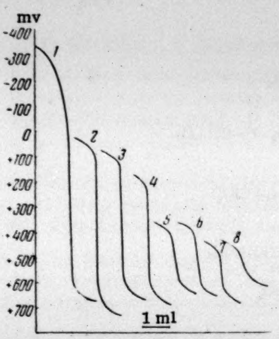


Fig. 1. Potentiometic titration curves for individual bases in a methyl ethyl ketone medium, the titrant being a solution of perchloric acid in the same solvent. 1) Tetraethylammonium hydroxide; 2) piperidine; 3) triethylamine; 4) o-phenanthroline; 5) benzimidazole; 6) tyramine; 7) acridine; 8) 3,5-dimethylpyrazole.

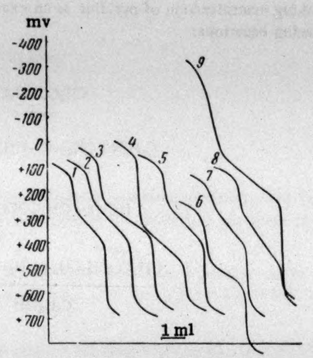


Fig. 2. Potentiometric titration curves of two-component mixtures in methyl ethyl ketone. 1) Triethylamine + o-phenathroline; 2) triethylamine + benzimidazole; 3) piperidine + benzimidazole; 4) piperidine + 3,5-dimethylpyrazole; 5) potassium hydroxide + o-phenanthroline; 6) tyramine + acridine; 7) tyramine + o-phenanthroline; 8) tyramine + 3,5-dimethylpyrazole; 9) tetraethylammonium hydroxide + tyramine.

Titration is carried out potentiometrically, using a glass electrode and a modified calomel electrode in a stream of dry nitrogen, which is passed into the titration beaker to prevent absorption of carbon dioxide and moisture from the air.

The titrant is added in 0.1-ml portions until the equivalent potential is established, after which it is added in 0.05-ml portions. Titration is continued until a constant potential is established.

The test bases possess different strengths in a methyl ethyl ketone medium (Fig. 1). The strongest base proved to be tetraethylammonium hydroxide, whose potential jump during titration was 700 mv (Curve 1). Piperidine and triethylamine (Curves 2 and 3 respectively) are weaker bases, their strengths being approximately equal. o-Phenanthroline proved to be even weaker (Curve 4). Benzimidazole (Curve 5) and tyramine (Curve 6) have approximately equal strengths in methyl ethyl ketone. The weakest bases are acridine (Curve 7) and 3,5-dimethylpyrazole (Curve 8).

Comparison of the titration curves of individual bases with titration curves of their mixtures showed that two bases can be titrated separately in their mixtures if the difference between the beginning of their potential jumps during titration of the individual bases is about 100 mv. Thus, the difference between the beginning of the jumps during titration of triethylamine (Fig. 1, Curve 3) and o-phenanthroline (Fig. 4, Curve 4) amounts to 100 mv.

The result of titrating a mixture of triethylamine and o-phenanthroline is shown in Fig. 2. The curve has two distinct potential jumps, the first corresponding to completion of the neutralization of triethylamine and the second to neutralization of o-phenanthroline.

Curve 2 (Fig. 2), which is the titration curve for a mixture of triethylamine and benximidazole, also has two potential jumps. The difference between the beginning of the potential jumps of these bases (Fig. 1) is 300 mv.

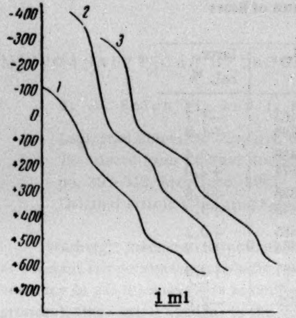


Fig. 3. Potentiometric titration curves for three-component mixtures in methyl ethyl ketone. 1) Potassium hydroxide + benzimidazole + p-aminoazobenzene; 2) tetraethylammonium hydroxide + tyramine + acridine; 3) tetraethylammonium hydroxide + tyramine + 3,5-dimethylpyrazole.

During titration of a mixture of piperidine and benzimidazole (Curve 3) a curve with two potential jumps is obtained, the jumps corresponding to completion of separate neutralization of piperidine and benximidazole. The remaining curves in Fig. 2 are also curves for titration of two-component mixtures: Curve 4 for a mixture of piperidine and 3,5-dimethylpyrazole, Curve 5 for potassium hydroxide and o-phenanthroline, Curve 6 for tyramine and acridine, Curve 7 for tyramine and o-phenanthroline, and Curve 8 for tyramine and 3,5-dimethylpyrazole. Two potential jumps are clearly observed on all the curves, the jumps corresponding to completion of the separate neutralization of the components of the mixture.

Fig. 3 shows the titration curve obtained on titrating a three-component mixture of bases. Curve 1 was obtained on titrating a mixture of potassium hydroxide, benzimidazole, and p-aminoazobenzene. The three distinct potential jumps show that each component of the mixture was titrated separately.

A curve with three potential jumps was obtained on titrating a mixture of tetraethylammonium hydroxide, tyramine, and acridine (Curve 2). The first jump corresponds to complete neutralization of tetraethylammonium hydroxide as the strongest base, the second to neutralization of tyramine, and the third to neutralization of acridine. Curve 3 was obtained on titrating a mixture of tetraethylammonium hydroxide, tyramine, and 3,5-dimethylpyrazole. The three components are again titrated separately even in this case. The first potential jump corresponds to complete neutralization of tetraethylammonium hydroxide, the second to tyramine, and the third to 3,5-dimethylpyrazole.

Table 1 contains the results obtained during quantitative determination of some organic bases by titration in a methyl ethyl ketone medium with a methyl ethyl ketone solution of perchloric acid. Individual bases can be determine by this method to an accuracy of 1%.

TABLE 1. Determination of Individual Bases by Titration in a Methyl Ethyl Ketone Medium

Test material	Sample wt., g	Found, g	Error, rel. %
3,5-Dimethylpyrazole	0,0800	0,0809	+1,0
o-Phenanthroline	0,0552	0,0557	+0,9
Tyramine base	0,0328	0,0328	0,0
Tetraethylammonium hydroxide	0,0814	0,0818	+0,4
Acridine	0,0460	0,0456	−0,9

The suitability of the suggested method for quantitative analysis of two- and three-component mixtures of bases is demonstrated in Table 2. The components of the mixtures can be determined to an accuracy of 1 to 3%.

SUMMARY

A new potentiometric method has been developed for the separate determination of bases in their mixtures; it is based on titration in a methyl ethyl ketone medium, using a solution of perchloric acid in the same solvent as titrant. Methyl ethyl ketone has the advantage over acetic acid as a solvent for test materials and as a titrating medium that it is possible to carry out separate titration of multicomponent mixtures of bases in it.

TABLE 2. Analysis of Two- and Three-Component Mixtures of Bases

Components	Sample wt., g	Found, g	Error, rel. %
Tyramine	0,0471	0,0463	—1,7
Acridine	0,0783	0,0798	+1,8
Tyramine	0,0428	0,0426	—0,4
3,5-Dimethylpyrazole	0,0526	0,0574	+2,0
Tyramine	0,0334	0,0328	+1,8
o-Phenanthroline	0,0473	0,0448	+3,0
Tetraethylammonium hydroxide	0,0484	0,0485	+0,2
Tyramine	0,0356	0,0364	+1,9
Tetraethylammonium hydroxide	0,0484	0,0487	+0,6
Tyramine	0,0282	0,0256	—2,1
Acridine	0,0642	0,0625	—2,8
Tetraethylammonium hydroxide	0,0484	0,0485	+0,2
Tyramine	0,0356	0,0364	+1,9
3,5-Dimethylpyrazole	0,0375	0,0384	+0,5

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MICROANALYTICAL HYDROGENATION

B. G. Belen'kii and I. S. Baraboshina

Leningrad Scientific Research Institute of Antibiotics

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Warburg's manometric method [1,2] permits determination of the amount of gas formed or used up in a system at constant temperature and volume, on the basis of changes in gas pressure. This method ensures a high experimental accuracy in gas microanalysis as compared with the volumetric method (measurement of changes in volume at constant pressure), since small changes in the volume of a gas in a system can be observed more readily by means of a manometric method than by direct change in volume. Thus Schwabe [3] has pointed out that the use of Warburg's technique permits changes in volume of a gas to be measured with an accuracy of ± 0.003 cm^3.

There are published references to the use of a manometric method of microanalytical hydrogenation. Kuhn and Moller [4] have developed a differential-manometric method of microhydrogenation, based on measurements of the difference in two vessels in which the test and a standard are hydrogenated under identical conditions. This method, which ensures and accuracy of measurement of ± 0.5% during a 40 hour hydrogenation using a 5-mg aliquot of test material, is rather difficult and complicated. Umbreit et al. ([1], p. 141) have developed a simple manometric method using standard Warburg apparatus for the analytical hydrogenation of pyridoxal, the accuracy being ±4%.

The present article is devoted to the development of a simple manometric method for microanalytical hydrogenation using a Warburg apparatus. We have succeeded in designing special hydrogenation cells and have developed a technique for catalytic heterogeneous hydrogenation, which makes it possible to carry out microanalytical determinations and to study the kinetics of the process indicated.

EXPERIMENTAL PART AND DISCUSSION OF RESULTS

a) Preparation of Purification of Hydrogen. The hydrogen used for hydrogenation was prepared electrolytically in an electrolyzer with Bruns's nickel electrodes [5]. The electrolyte was a solution of 200.0 g KOH and 50.0 g $Ba(OH)_2$ in 500 ml of water. The hydrogen formed after a preliminary drying over $CaCl_2$ was freed from traces of oxygen in a tube packed with palladinized asbestos heated at 300-350°, and from traces of H_2S in a wash bottle containing 20% NaOH solution saturated with PbO. The gas was next freed from splashes of alkali solution in a splash head and in a tube filled with glass wool, and finally in a $CaCl_2$ tube.

b) Modification of Warburg Apparatus for Hydrogenation. We used Warburg apparatus produced by the "Labor" firm (Hungary) for studying cell respiration. This apparatus consists of a water thermostat with a turbine stirrer and a mercury-toluene thermoregulator which ensures that the temperature in the bath can be kept to an accuracy of ± 0.05° over the range 20-80°. Oscillating panels with a maximum number of oscillations of 260 per min are fitted to the side walls of the thermostat. The amplitude and oscillating rate are readily regulated. Warburg manometers, connected via ground joints to vessels which are immersed in the water thermostat, are fitted by means of special clips to the panels.

In the course of our work we became convinced, despite Umbreit's ([1], p 141) directions regarding the use of a standard system of Warburg respirometers for microanalytical hydrogenation, that they suffer from the following disadvantages which hinder their use: 1) because of the low depth of the retort, the material being hydrogenated is thrown out prematurely into the working space of the vessel during saturation of the catalyst with hydrogen; 2) during oscillation (shaking), the catalyst collects on the bottom of the vessel and is thereby withdrawn from the reaction; 3) grease from the ground joint falls into the hydrogenzation vessel; 4) it is very difficult to replace the air completely by hydrogen even when the hydrogen is passed for a long time through the manometer into the Warburg vessel; 5) it is impossible to control the extent to which the catalyst is saturated with hydrogen during an experiment.

Taking all these drawbacks into account, we have modified the standard Warburg apparatus and adapted it for hydrogenation (Fig. 1). The working space of the vessel we used is a horizontal semicylinder with a flat bottom 1, the axis of the cylinder lying along the direction of oscillation. To the cylinder is connected a vertical tube 2 ending in an external ground joint 3 which prevents any grease getting into the vessel. A tube 4 is fused into the vertical part of the vessel at an angle of 60°; to this tube is connected a deep retort 5 which also has a ground joint and can be rotated. The ground joint of the retort is provided with a channel 6 which prevents any grease from passing inside the hydrogenation vessel.

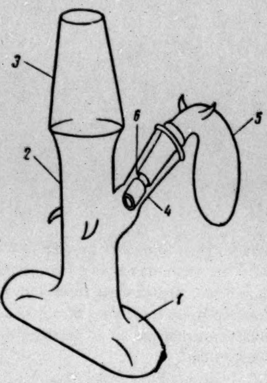

Fig. 1. Hydrogenation vessel. 1) Horizontal section; 2) vertical tube; 3) ground joint; 4) side tube with ground joint; 5) rotating retort; 6) channel.

The joints are lubricated with vacuum grease obtained by melting vaseline, paraffin, and natural rubber in the proportions 5 : 2:5. The design of the manometer was also modified to some extent (Fig. 2). To the rubber tube 2 was connected a two-way tap 3, connected by a rubber hose with the glass reservoir 5. This construction made it possible to evacuate the manometric liquid (mercury) from the manometer, and after covering the tap 3 to suck out the gas from the system by means of a water pump, and then fill the system with hydrogen through the three-way tap 6. Five successive evacuations and fillings of the system with hydrogen made it possible to remove the air completely from the system and to ensure a hydrogen atmosphere. Tap 3 was then closed, the reservoir plus rubber tube disconnected, and the apparatus placed in its original position. This was done by turning the screw clip while the manometer was fitted onto the Warburg vessel, and with the three-way tap open the level of the manometric liquid in both arms of the manometer was adjusted to the null point (a mark at 250 mm). The three-way tap was then closed, an experiment carried out, and the pressure change in the system measured from the change in the level of the manometric liquid in the left arm after the system had been adjusted to constant volume–setting the level of the manometric liquid at the null point in the right arm. The manometer readings were corrected by a so-called thermobarometer– the usual type of manometer with a Warburg vessel filled with the solvent used in the reaction, and operating under the same conditions as those in the working manometer. The latter makes it possible to take into account the effect of temperature changes in the bath and the surrounding air, and also of atmospheric pressure, on the change in gas pressure in the system during an experiment.

c) Measurement of the Volume of the Hydrogenation Vessel. The volume of the hydrogenation vessel and of that part of the manometer up to the null point was determined by a method described by Umbreit ([1], p.85); this consists in weighing the mercury required to fill the space indicated.

d) Calculation of the Amount of Hydrogen Absorbed. The hydrogen used is calculated by means of the formula given in [1], p. 13:

$$x = \left[\frac{(V - V_1)\frac{273}{T} + V_1\alpha}{P_0}\right] h = Kh, \tag{I}$$

where V is the volume of the hydrogenation vessel and the working part of the manometer, ml; V_1 is the volume of liquid in the vessel, ml; α is the solubility of hydrogen in the liquid, mg / ml at normal pressure; T is the experimental temperature in degrees absolute (273 + t°); P_0 is normal pressure (mm of the manometric liquid); h is the decrease in pressure in the system during an experiment (mm of manometric liquid); x is the amount of hydrogen used, ml; K is the vessel constant. Since $P_0 = \frac{760 \cdot 13.60}{d}$, where 760 is normal pressure in mm Hg, 13.60 is the sp. gr. of mercury, and d is the specific gravity of the manometric liquid, on the basis of equation I it is possible to write:

$$K = \frac{x}{h} = \frac{\left[(V - V_1)\frac{273}{T} + V_1\alpha\right] d}{760 \cdot 13{,}60} \tag{II}$$

and, where mercury is the manometric liquid

$$K = \frac{(V - V_1)\frac{273}{T} + V_1\alpha}{760}. \qquad \text{(III)}$$

Since all the values which enter into formula II are constant for a given experiment, determination of the gas used reduces to multiplying the value of the vessel constant K by the change in the level of the manometric liquid h.

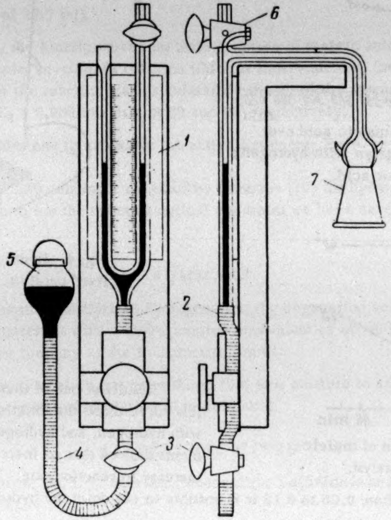

Fig. 2. Modified manometer. 1) U-shaped manometer tube; 2) rubber tube; 3) three-way tap; 4) rubber hose; 5) glass reservoir; 6) three-way tap; 7) outlet tube with ground joint for connecting to hydrogenation flask.

It also follows from formula II that the value of K characterizes the sensitivity of the hydrogenation apparatus. In order to increase the sensitivity of the apparatus the vessel constant K should be lowered. Of particular importance is the decrease in specific gravity of the manometric liquid, since a change of d from 13.60 (mercury) to 0.80 (96° ethanol) increases the sensitivity of the method 17 times without any need for altering the construction and geometrical parameters of the hydrogenation cell.

e) Hydrogenation of Maleic Acid over Palladium Oxide. The efficiency of the apparatus developed was checked by hydrogenating maleic acid which had been recrystallized three times from twice-distilled water. Palladium oxide was prepared by Adams's method [6]. A suspension of 0.7-1.6 mg of PdO in 1 ml of twice-distilled water was placed in the operating part of the hydrogenation vessel (see Fig. 1); a solution of 11.8-12.6 mg of maleic acid in 1.2 ml of twice-distilled water was introduced into the side retort. The system was filled with hydrogen and the catalyst saturated with hydrogen by shaking the flask 100-120 times per minute. After hydrogen had ceased to be absorbed by the palladium oxide, the level of the mercury in both arms of the manometer was adjusted to the null point, after which the retort containing the maleic acid solution was turned over and hydrogenation of the maleic acid carried out at the maximum shaking rate of 240-260 oscillations per minute, the path of the reaction being followed by observing the decrease of hydrogen pressure in the system. Completion of hydrogenation is assessed from cessation of hydrogen absorption. The experiments were carried out at 40 ± 0.05°.

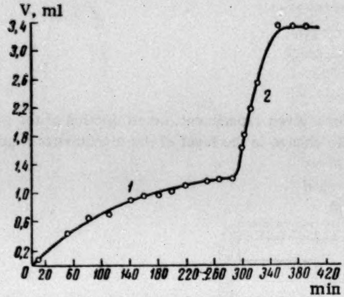

Fig. 3. Hydrogenation of maleic acid over PdO. 1) Saturation of catalyst with hydrogen; 2) hydrogenation of maleic acid.

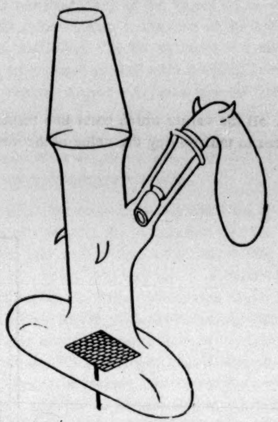

Fig. 4. Hydrogenation vessel with fixed catalyst.

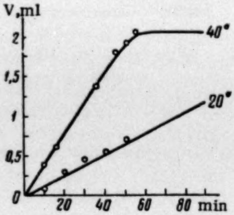

Fig. 5. Hydrogenation of maleic acid over a Pd-Cu catalyst.

Results of one of these experiments are shown in Fig. 3; this curve shows the kinetic curves of the saturation of catalyst with hydrogen, and hydrogenation of maleic acid. Measurements showed that an increase in the amount of PdO favors an increase in reaction rate. Thus by altering the proportion by weight of PdO and maleic acid from 0.05 to 0.13 it is possible to cut down the hydrogenation time from 165 to 60 min.

Good reproducibility of results was observed in the experiments described; they did not differ from each other by more than 0.4%, while the deviation from the theoretical value of the hydrogenation equivalent was 0.4-0.8% when 2.21-2.26 ml of hydrogen was used up in a vessel with a volume of 25.34 ml.

f) Study of the Kinetics of Hydrogenation of Maleic Acid over a Copper-Palladium Catalyst. As is evident from Fig. 3, the kinetic curve of the hydrogenation of maleic acid over PdO is of the first order. This regularity could be both a reflection of the true character of the catalytic process, and a result of diffusion complications developing on the catalyst surface. Support for the latter hypothesis comes from published references [7-9] to the fact that hydrogenation of maleic acid over palladium contacts is of zero order. In order to check on the possibility of using the suggested method for studying the kinetics of hydrogenation, we tried to eliminate diffusion complications. For this purpose we increased the shaking rate from 270 to 400 oscillations per min (requisite modifications were made to the Warburg apparatus). This increase in shaking rate, however, led to the catalyst being thrown into the vertical part of the hydrogenation vessel, and to its withdrawal from the sphere of reaction; accordingly, we decided to fix the catalyst in the working part of the vessel. The catalyst was used in the form of black placed on a platinum disc or grid with an area of 1.7 cm^2 fused into the horizontal part of the hydrogenation flask (Fig. 4). Instead of PdO we use a palladium-copper alloy containing 30 atomic % of Cu recommended by Tverdovskii and Kaprova [9]. This catalyst possesses a high activity in the hydrogenation of ethylene and acetylene bonds and is less likely to be poisoned than pure Pd. The Pd-Cu alloy was prepared by electrolytic deposition from a bath consisting of a mixture of the following solutions: I) 0.200 g $PdCl_2 \cdot 2H_2O$ and 0.250 g $NaNO_2$ in 10 ml H_2O; II) 0.14 g $CuSO_4 \cdot 5H_2O$ and 0.360 g $(NH_4)_2SO_4$ in 10 ml H_2O; III) 0.14 N H_2SO_4 in a ratio by volume of I : II : III = 5.9 : 4.1 : 30. The deposition time was varied from 3 to 10 min at a current density of 70 ma/cm^2. The precipitate of copper-palladium black was washed with water and subjected to cathodic purification for removing adsorbed ions at current of 70 ma/cm^2 in the course of 30 min in

0.1 N HCl or 0.05 N H_2SO_4. Maleic acid was hydrogenated at 20 and 40° (± 0.05°) by the technique described above. The kinetic curve of absorption of hydrogen by the Pd-Cu catalyst is similar to the curve shown in Fig. 3 for PdO. When the Pd-Cu catalyst is used, the amount of hydrogen required for saturating the catalyst is almost five times the amount required for hydrogenating the maleic acid. This latter fact indicates the need for careful control of the saturation of catalyst with hydrogen during microanalytical hydrogenation. As in the case of PdO, it was observed that the larger amount of hydrogen used for saturating the catalyst, i.e., the greater the amount of catalyst taken for an experiment, the more rapid is the hydrogenation process. Kinetic curves for the hydrogenation of maleic acid are shown in Fig. 5. Results with good reproducibility were again obtained in these experiments (± 0.1%, with a deviation from the theoretical value of the hydrogenation equivalent of +0.4% when 2.04-2.14 ml of hydrogen was used in a vessel with a volume of 27.7 ml).

As is evident from Fig. 5, the kinetic curves for hydrogenation of maleic acid over a Pd-Cu catalyst have a shape characteristic of a zero order reaction (a reaction which is independent of the velocity constant and concentration). The velocity constants of the reaction was calculated by means of the formula: $K = \Delta x / \Delta t$ and were found to be $K_1 = 0.014$ ml/min and $K_2 = 0.039$ ml/min at 20 and 40° respectively.

The results obtained enables one to calculate the activation energy $E_A = \frac{4.575 \Delta \ln K}{\Delta T^{-1}} = 9250$ cal/mole, which lies within the limits 1000 to 10 000 cal/mole obtained by Kobozev [10] for hydrogenation of ethylene derivatives. This indicates that it is possible to use the microanalytical apparatus we have developed for studying the kinetics of the hydrogenation process.

SUMMARY

An improved apparatus for microanalytical hydrogenation (hydrogenation vessels and manometers) permits quantitative hydrogenation of materials with a hydrogenation equivalent of about 100 with a accuracy of ± 0.5%, using a 10-mg sample, and using mercury as the manometric liquid.

Taking maleic acid as an example, it has been shown that it is possible to apply the improved apparatus to study of the kinetics of the catalytic hydrogenation of maleic acid.

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THE DECOMPOSITION OF ORGANIC COMPOUNDS IN A RAPID STREAM OF OXYGEN UNDER THE CONDITIONS OF MICROELEMENTAL ANALYSIS

V. A. Klimova and T. A. Antipova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR, Moscow

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It has been assumed that during rapid methods of analysis by combustion in a gas stream [1] the material is first of all subjected to pyrolytic decomposition in the quartz test tube inserted in the combustion tube. It has been considered [2] that there may occur in the decomposition zone, firstly tarring and coking of the material with loss of hydrogen and formation of a difficultly volatile resin, and secondly, splitting with formation of active fragments.* In order to confirm experimentally that such processes do in fact occur, we carried out interrupted combustion of test materials (i.e., discontinuous combustion) The first time that the decomposition process was interrupted was when visible changes in the material were detected; at this stage either qualitative tests were carried out for aldehydes and unsaturated compounds in the residue, or the residue and the apparatus used for absorbing carbon dioxide and water were weighed. From one to three interruptions were made during each experiment.

As one might have expected, during combustion of hydrobarbons we were able to detect qualitatively formation of aldehydes and unsaturates at the very beginning of combustion; this confirmed our assumption of the development of active fragments during decomposition.

Determination of water and carbon dioxide at various stages of the process enabled us to assess the changes in the proportion between carbon and hydrogen both in the residue and in the decomposition products. We expected to find that these proportions would differ sharply from the proportions for the original compound. Nevertheless, experiments with hydrocarbons, acids, alcohols, and ethers showed that this is not so. Actually, in almost all cases, the proportions of carbon and hydrogen in the original material and in the products of incomplete decomposition and in the residue were very close to each other. The only exceptions were compounds which split off water at comparatively low temperatures, e.g., sugar, crystallohydrates, etc. A curious feature was the fact that even when the residue in the quartz test tube appeared to be completely resinified, the proportion of hydrogen and carbon remained almost the same. Accordingly, resinification which is observable visually only proceeds to a small extent, although it leads to coloration of the residue.

All these facts lead one to think that combustion appears to proceed in layer fashion, in which each portion of material passes into the gaseous state on heating, then burns up completely, breaking down beforehand to form active fragments. This may occur both with participation of oxygen (formation of aldehydes during combustion of hydrocarbons) and without participation of oxygen (formation of unsaturates). It should be pointed out that similar results were obtained on varying the size of the quartz test tube used for combustion, even in the case when the size of the test tube enabled the decomposition of the whole mass of sample to occur at once.

Thus the suggestion which we made previously that decomposition in the test tube (preliminary pyrolysis) is accompanied by resinification of test material and splitting off of hydrogen was not confirmed. Formation of active fragments was confirmed experimentally. Accordingly, combustion in a test tube does not resolve into pyrolysis and oxidation stages, but proceeds, as usual, in accordance with the theory of combustion.

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* By active fragments we mean thermal decomposition products which are more reactive than the original test material, e.g., aldehydes, unsaturated free radicals, hydrogen, etc.

EXPERIMENTAL

Combustion was carried out in the usual apparatus [1]. The test material was decomposed in a quartz test tube 50-70 mm long and with an internal diameter of 6-7 mm by gradually moving the burner from the open end of the test tube to its closed end, i.e., counter to the oxygen stream (20-40 ml/min). Combustion products were trapped and weighed as usual.

TABLE 1

Test Material	Degree of pyrolysis	Color	Presence of aldehydes
Paraffin	Not subjected to decomposition	None	None
"	To a light-yellow color	Dense violet	Present
"	To a dark-yellow color	Violet	"
"	Combustion almost to completion	None	None
$C_{28}H_{58}$	Not subjected to decomposition	"	"
"	To a light-yellow color	Violet	Present
$C_6H_5(CH_2)_3CH_3$	Ditto	"	"
Naphthalene	"	None	None
Benzene	"	"	"

TABLE 2

Solution to which a solution of $SbCl_3$ in chloroform was added	Color with $SbCl_3$	Presence of unsaturates
Chloroform	None	Absent
Paraffin dissolved in chloroform	"	"
Cinammic aldehyde in chloroform	Brown	Present
Paraffin taken to a weak-yellow color and dissolved in chloroform *	Ditto	"
Paraffin taken to a yellow color and dissolved in chloroform*	"	"

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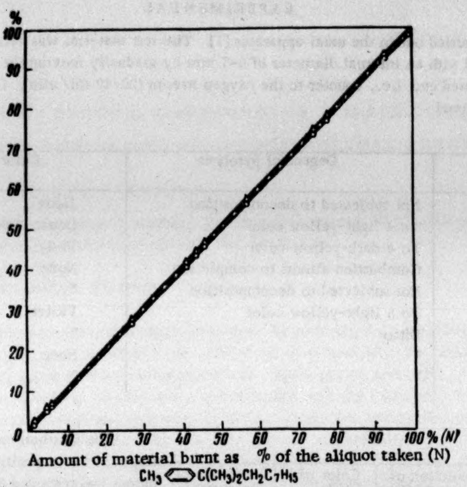
* Before addition of the antimony trichloride solution, the test samples only had a weak yellow color which did not change over a period of 6 hours.

The combustion was interrupted at various stages of decomposition. At the interruption the burner was removed and the combustion products expelled into the apparatus for absorbing water and carbon dioxide. After the interruption the residue of incompletely decomposed material in the test tube was tested for the presence of unsaturates and aldehydes in it, or the absorption apparatus was weighed; this was subsequently reconnected to the combustion tube, and combustion continued to completion or to the next interruption.

Qualitative Tests for Aldehydes. The residual material in the test tube used for decomposition was dissolved in chloroform and the solution transferred to a test tube. A freshly prepared solution of fuchsin sulfurous acid, which acquires a violet color in the presence of aldehydes, was added to the chloroform solution. From the results given in Table 1 it is clear that decomposition of aliphatic hydrocarbons is accompanied by formation of aldehydes.

Qualitative Tests for Unsaturates. The residual material in the test tube used for decomposition was dissolved in chloroform and the solution transferred to an ordinary test tube. To this solution was added a 30% solution of antimony trichloride in chloroform; in the presence of unsaturated compounds this solution turns brown. As the results in Table 2 show, decomposition of paraffin is accompanied by formation of unsaturates.

Determination of Carbon and Hydrogen at Various Stages of the Decomposition. On the basis of the results obtained on weighing the absorption apparatus after each interruption, the content of carbon and hydrogen in the burned-out part of the aliquot was calculated in relative percentages. Tables 3 and 4 contain some results of several combustions of various samples of each material. During combustion of one sample, 2-3 interruptions were made, as far as possible at different stages of decomposition. The tables indicate all the experiments carried out with a given test material, the results being arranged in order of increasing amount of the burned-out part of the sample of test material. The ratio of the percentage content of hydrogen to carbon indicates that the decomposition process occurs in layer fashion. Actually, it is only for materials which readily split off water that this ratio is greater than unity (Table 4); in all remaining cases it is almost equal to unity.



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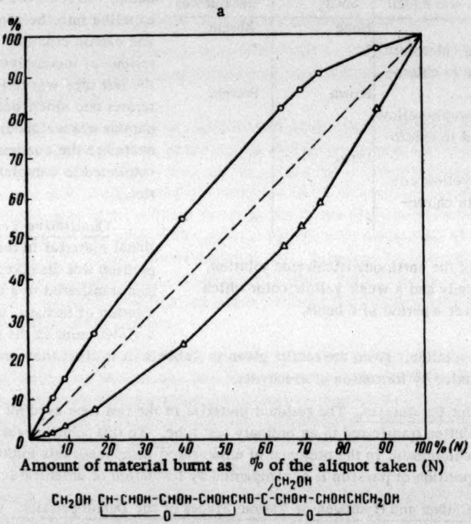


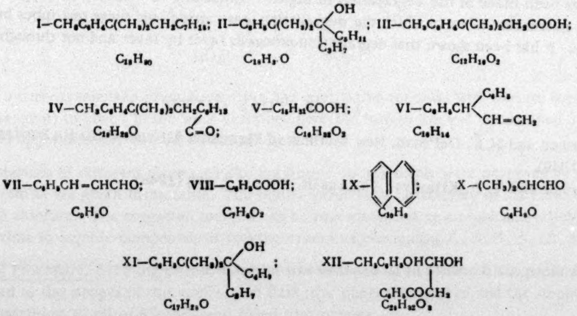
Sucrose

b

Curves for typical cases of burning of compounds during combustion with pyrolysis in the test tube used for decomposition. a) Test material which is not dehydrated on heating; b) material which is readily dehydrated on heating.

TABLE 3

Test substance	Amount, %		H/C	Test substance	Amount, %		H/C	Test substance	Amount, %		H/C
	C	H			C	H			C	H	
I	1,73	1,88	1,08	V	0,65	1,87	2,81	IX	18,12	19,48	1,07
	5,16	5,78	1,12		3,63	4,80	1,32		30,70	29,99	0,98
	6,18	6,26	1,01		10,88	14,83	1,36		73,03	75,94	1,04
	26,71	27,74	1,04		19,70	23,00	1,17		99,18	99,53	1,00
	40,75	41,91	1,02		30,23	31,69	1,05		100	100	1,00
	43,51	44,36	1,02		46,72	49,87	1,07				
	56,37	57,58	1,02		66,26	67,35	1,01				
	73,81	74,74	1,01		78,36	89,34	1,14				
	77,16	78,92	1,02		94,85	97,48	1,02				
	92,65	93,24	1,01		100	100	1,00				
	100	100	1,00								
II	0,76	1,30	1,71	VI	52,33	56,54	1,08	X	76,13	76,28	1,00
	17,00	18,04	1,01		61,15	64,72	1,06		89,98	89,77	0,99
	28,49	30,42	1,07		69,86	74,91	1,07		91,86	91,24	0,99
	43,60	46,34	1,06		100	100	1,00		100	100	1,00
	79,97	80,07	1,00								
	88,23	89,11	1,01								
	100	100	1,00								
III	0,90	1,66	1,84	VII	36,10	39,86	1,10	XI	9,75	11,68	1,20
	19,15	18,88	0,98		45,84	49,80	1,08		20,59	21,39	1,04
	25,49	24,66	0,96		54,06	57,63	1,07		47,92	49,77	1,03
	36,10	36,88	1,02		79,73	83,56	1,04		56,21	56,33	1,00
	44,03	44,11	1,00		100	100	1,00		82,40	82,62	1,00
	59,93	60,00	1,00						100	100	1,00
	88,81	90,94	1,02								
	100	100	1,00								
	28,88	30,96	1,07	VIII	2,78	5,77	2,08	XII	13,83	23,70	1,71
	37,47	40,07	1,04		31,68	31,96	1,00		31,80	37,83	1,19
	43,24	44,02	1,02		62,04	60,50	0,97		53,64	58,33	1,09
	59,12	57,63	0,96		99,61	97,54	0,98		74,60	78,09	1,04
	71,91	72,64	1,00		100	100	1,00		91,05	93,04	1,02
	95,24	95,60	1,00						100	100	1,00
	100	100	1,00								



I—$CH_3C_6H_4C(CH_3)_2CH_2C_7H_{15}$; II—$C_6H_5C(CH_3)_2C(OH)(C_5H_{11})(C_3H_7)$; III—$CH_3C_6H_4C(CH_3)_2CH_2COOH$;

$C_{18}H_{30}$ $C_{18}H_{30}O$ $C_{12}H_{16}O_2$

IV—$CH_3C_6H_4C(CH_3)_2CH_2C_6H_{12}C{=}O$; V—$C_{15}H_{31}COOH$; VI—$C_6H_5CH(C_2H_5)(CH{=}CH_2)$

$C_{18}H_{28}O$ $C_{16}H_{32}O_2$ $C_{11}H_{14}$

VII—$C_6H_5CH{=}CHCHO$; VIII—C_6H_5COOH; IX—; X—$(CH_3)_2CHCHO$

C_9H_8O $C_7H_6O_2$ $C_{10}H_8$ C_4H_8O

XI—$C_6H_5C(CH_3)_2C(OH)(C_4H_9)(C_3H_7)$; XII—$CH_3C_6H_3OHCHOH(C_6H_4COCH_3)$

$C_{17}H_{28}O$ $C_{21}H_{22}O_3$

Since in the course of a study of the decomposition of more than 24 different materials only the two types of decomposition indicated were observed, it can be fairly safely assumed that combustion in the quartz test tube proceeds layer by layer and not through the whole mass of the sample of compound being burned.

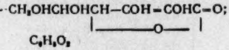
TABLE 4

Test substance	Amount, %		H/C	Test substance	Amount, %		H/C	Test substance	Amount, %		H/C
	C	H			C	H			C	H	
I	1,75	7,70	4,40	III	0,33	2,42	7,33	V	0,50	12,46	24,92
	1,83	10,22	5,58		0,85	9,75	11,47		0,69	12,96	18,78
	3,58	15,08	4,21		2,56	15,26	6,00		1,11	14,10	12,88
	7,40	26,28	3,55		11,17	45,86	4,10		2,94	27,56	9,37
	23,81	54,81	2,30		22,22	66,37	2,99		4,83	33,72	7,00
	47,85	82,00	1,71		61,53	92,55	1,50		6,57	35,71	5,43
	52,56	86,47	1,64		100	100	1,00		15,83	50,55	3,20
	58,18	90,19	1,55						26,62	55,70	2,10
	81,49	96,73	1,11						35,60	64,44	1,82
	100	100							80,24	87,85	1,09
									93,37	95,34	1,09
									100	100	1,00
II	4,07	65,94	16,20	IV	6,49	2,13	0,33	VI	0,12	2,34	19,50
	5,50	67,28	12,23		2,77	5,47	2,00		0,51	4,00	7,84
	14,03	70,93	5,05		12,57	22,65	1,82		1,27	5,63	4,43
	71,33	88,60	1,24		31,75	44,27	1,08		1,55	11,44	7,39
	88,93	95,38	1,07		54,37	64,99	1,19		9,45	14,82	1,57
	100	100	1,00		58,00	71,01	1,22		18,76	21,37	1,14
					69,88	75,71	1,08		31,15	33,74	1,08
					99,64	94,75	0,95		48,65	56,52	1,20
					100	100	1,00		69,37	70,13	1,01
									100	100	1,00

I—Sucrose; $C_{12}H_{22}O_{11}$

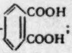
II—$HOOC-COOH \cdot 2H_2O$; $C_2H_6O_6$

III—



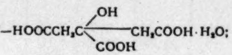
$CH_2OHCHOHCH-COH=COHC=O$; $C_6H_8O_6$

IV—



; $C_8H_6O_4$

V—



$HOOCCH_2C(OH)(COOH)CH_2COOH \cdot H_2O$; $C_6H_{10}O_8$

VI—$HOOCCH=CHCOOH$ $C_4H_4O_4$

SUMMARY

A study has been made of the degradation of organic compounds in a stream of oxygen; the test compounds were inserted in quartz test tubes in which the degradation was carried out, these test tubes being inserted in an empty combustion tube. It has been shown that degradation proceeds layer by layer and not throughout the whole mass of the compound.

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A MICROMETHOD FOR THE DETERMINATION OF SULFUR IN ORGANIC MATERIALS USING A NEW INDICATOR, CARBOXYARSENAZO, FOR TITRATION OF SO$_4^{2-}$ IONS

K. F. Novikova, N. N. Basargin, and M. F. Tsyganova

Ya. V. Samoilov Scientific Institute of Fertilizers and Insectofungicides, Moscow, and V. I.
Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

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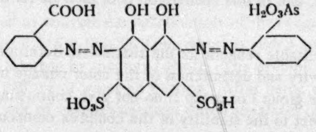
Among the methods for determining sulfur in organic compounds the ones which have found widest application are catalytic destructive hydrogenation [1], pyrolytic combustion in an oxygen stream [2], and also a number of methods which include decomposition of organic material by Schöniger's method [3-7]. When such methods are used, determination of the sulfate ion formed is usually carried out by titration with a solution of a barium salt in the presence of indicators [3-5].

A large number of organic reagents of different classes have been suggested as indicators for barium [3-5, 8-12]. Neverthless, application of the widely used indicators for barium such as sodium alizarin sulfonate [4], thoron [5], phthalein complexon [3,8], sodium rhodizonate [10,11], stilbinaphthazo [12], etc., to titration of sulfate ions is not characterized by high sensitivity and by clearly defined color changes. In this connection, a new organic reagent is suggested in the present article for the titrimetric determination of sulfur after combustion of test material by the Schöniger method; this reagent* is carboxyarsenazo, 2-phenylcarboxylic acid-(1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid-(7-azo-1)-2-phenylarsonic acid



At pH 5.5-6.5 carboxyarsenazo gives a sensitive and contrasting reaction with barium ions. The color change is from raspberry (reagent) to blue. In the work described here the sulfate ion was determined by direct titration with barium nitrate in an approximately 50% ethanolic medium.

Organic compounds of different classes containing from 8 to 35% sulfur were analyzed by the technique suggested. Experimental results are given in the table. The results were fairly satisfactory in all cases. The experimental accuracy is ± 0.25% absolute. The suggested method can be recommended as a rapid and reliable method for routine determination of sulfur in organic compounds of varying structures containing C, H, O, N, Cl, and S.

Experimental Procedure. 5-10 mg of test material was wrapped up in ashless filter paper and placed in a platinum basket attached to the stopper of the combustion flask; the paper was ignited and the stopper plus sample inserted in a flask containing 10 ml of 6% H_2O_2 and filled with oxygen.

Thirty to forty minutes after combustion, the solution in the flask was evaporated down to a volume of 10 ml; it was cooled and 25 ml of ethanol and 10 ml of an acetate buffer solution with pH 5.5-5.6 were added. The solution was finally titrated with 0.02 N $Ba(NO_3)$ solution in the presence of two drop of a 0.3% aqueous solution of carboxyarsenazo until the violet color changed to a pale blue.

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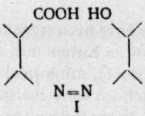
* The reagent was synthesized in GEOKhI, Academy of Sciences, USSR, by N. N. Basargin.

Test material	S content, %		Test material	S content, %	
	calc.	found		calc.	found
p-$NH_2C_6H_4SO_3H$	18,49	18,52 18,60 18,46	$CH_3SO_2N(SCCCl_3)C_6H_4CH_3$	19,13	19,31 19,35 19,24
p-$ClC_6H_4SO_2NH_2$	16,71	16,61 16,81 16,66	$C_6H_5CH_2SCH_2C_6H_5$	14,95	15,15 15,13
$(CH_3)_2NSO_2Cl$	22,37	22,35	$ClSCCl_3$	17,20	17,11 17,09 17,08
p-$NH_2C_6H_4SO_2NH_2$	18,61	18,73 18,73 18,74	Methylene blue	8,59	8,52 8,38
			$C_2H_5OCSSCH_2COOH$	35,60	35,80 35,49

The barium solution was standardized against 0.02 N H_2SO_4. Phosphates interfere with the determination.

Properties of Carboxyarsenazo. The reagent has two functional analytical atomic groups:



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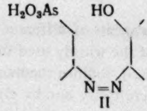

II

which occur separately in a number of reagents suggested by Kuznetsov [13,14]. In contrast to the reagent arsenazo III [15] which has two type II groups in its molecule, carboxyarsenazo forms comparatively unstable complexes with an unlimited number of metal ions, and in this connection is of interest for the complexometric determination of barium and other elements.

Carboxyarsenazo is a more suitable reagent for the titrimetric determination of sulfate ions than the reagents listed above with respect to sensitivity and definiteness of the color change in the case of barium. It should be noted that reagents having only one group I or group II do not give contrasting color reactions with barium ions, even in an alkaline medium. With respect to the stability of the complex compounds formed with the elements, carboxyarsenazo occupies an intermediate position between the reagents arsenazo and arsenazo III.

Carboxyarsenazo is a crystalline dark-violet powder, stable in the dry state and in aqueous solutions. A solution of the reagent in an acid medium has a raspberry color, while its solution in alkali is blue, and in concentrated H_2SO_4 green. The color change of the reagent in alkalis, concentrated H_2SO_4, and during complex formation with different elements is in good agreement with published results [16].

Light absorption curves of the reagent and of its compound with barium are shown in Fig. 1. The absorption curve of the complex with barium has two maxima at 590 and 650 mμ respectively. The molar extinction coefficient of the complex at pH 5.5 and 590 mμ is 29 200.

The effect of pH on the color of the reagent itself and on its complex with barium is shown in Fig. 2. The optimum conditions for titrating with carboxyarsenazo are pH 5.5-6.5 in the acid region and pH 9-10.5 in the alkaline region.

Synthesis of Carboxyarsenazo.* Carboxyarsenazo was prepared by azo coupling of the diazonium compound of anthranilic acid with chromotropic acid in a bicarbonate medium, followed by a further coupling of the isolated

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* The reagent is produced by the Voikov Moskhim Plant.

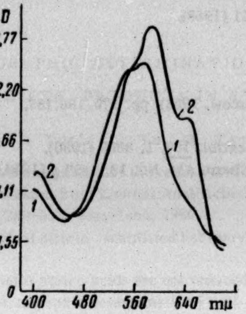

Fig. 1. Light absorption curves of a $1.8 \cdot 10^{-5}$ M solution of carboxyarsenazo (1) and of its complex with barium (2) at pH 5.5. SF-4 spectrophotometer, cell 10 mm.

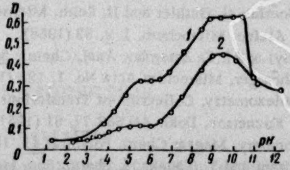

Fig. 2. Effect of pH on the development of the color of the barium-carboxyarsenazo complex (1). Barium concentration $5.4 \cdot 10^{-5}$ M. Carboxyarsenazo solution $1.8 \cdot 10^{-5}$ M (2). SF-4 spectrophotometer, cell 10 mm, λ = 650 mμ.

monoazo product [2-phenylcarboxylic acid-(1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] with the diazonium compound of o-aminophenylarsonic acid. The second stage of the synthesis was carried out using the technique of increasing the reactivity of the material by complex formation [16].

13.02 g (0.06 M) o-aminophenylarsonic acid is dissolved in 20 ml of water and 15 ml of concentrated HCl. The solution is cooled and then diazotized by adding 4.5 g (0.065 M) $NaNO_2$ in 10 ml of water with stirring.

10.24 g (0.02 M) of the disodium salt of the monoazo product is dissolved in 70 ml of water, 1.5-1.7 g of CaO being added. First the diazo solution and then CaO (in portions of about 0.2 g, total 20 g) are added periodically to the solution obtained on cooling and stirring.

The reaction mixture, which is dark-blue in color, is stirred for 40-60 min and allowed to stand overnight. It is then acidified with 40 ml of concentrated HCl; the precipitate of the calcium salt of carboxyarsenazo is filtered off and washed with 50 ml of 6 N HCl. The yield is 14-15 g.

In order to purify the product and to convert the calcium salt of the reagent to its sodium salt, 14.5 g of the product is dissolved in 100 ml of water; 4.5-5 g Na_2CO_3 (anhydrous) is added and the solution heated and then filtered. The reagent is salted out of solution by means of NaCl. The precipitate of the trisodium salt of the reagent is filtered off and dissolved in 250 ml of water on heating. After being cooled, the solution is acidified with HCl to pH about 1, and the disodium salt of carboxyarsenazo which separates out filtered off. The yield of pure product is 11-12 g.

Carboxyarsenazo can also be obtained by a similar method by azo coupling of arsenazo with the diazonium compound of anthranilic acid.

SUMMARY

A titrimetric micromethod for the determination of sulfur in organic compounds has been developed. Test material is decomposed by the Schöniger technique in a flask filled with oxygen, and the sulfate ions formed titrated with a barium nitrate solution using a new indicator, carboxyarsenazo. The synthesis and properties of carboxyarsenazo are described. The analytical accuracy is ± 0.25% (absolute).

Phosphorus present in the test material interferes with sulfur determination.

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POLAROGRAPHIC DETERMINATION OF CAPROLACTAM AND AMINO ACIDS–INTERMEDIATE PRODUCTS IN SYNTHETIC FIBER PRODUCTION

Ya. I. Tur'yan, Yu. M. Tyurin, and B. P. Zhantalai

Lisichansk Branch of the State Scientific Research and Planning Institute of the Nitrogen Industry

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Aliphatic amino acids are not reduced on a dropping mercury electrode, but several indirect methods are known for their polarographic determination [1-3].

Caprolactam and amino acids–intermediate products in synthetic fiber production–have not hitherto been studied polarographically. The work described here is devoted to the development of a method for the polarographic determination of these amino acids (AA). In this method caprolactam (CL) was converted into ϵ-aminocaproic acid (ACA) by hydrolysis(at a concentration $C_{CL} \leq 2$ g caprolactam in 1 liter of about 1 N H_2SO_4, caprolactam is completely hydrolyzed after boiling for one hour under reflux).

Among other amino acids which are important for synthetic fiber production we studied 7-amino enanthic acid (AEA), 9-aminopelargonic acid (APA), and 11-aminoundecanoic acid (AUA).

EXPERIMENTAL*

The basis of the polarographic method which we have developed for the determination of amino acids is the reaction between amino acids and formaldehyde (F) in alkaline media [4]:

$$NH_2RCOO^- + CH_2O \overset{K'_{\text{equilib.}}}{\leftrightarrows} CH_2RCOO^- + H_2O. \quad (1)$$

The compound CH_2NRCOO^- – a so-called Schiff's Base (SB) formed as the result of the reaction is polarographically active; it gives one clearly defined polarographic wave at all values of the pH of the supporting electrolyte; the wave appears at potentials which are more positive than that of the formaldehyde wave. This is a very important factor, since a large excess of formaldehyde is used for carrying out the reaction.

It should be pointed out that Zuman [5] was the first to establish the possibility of carrying out a polarographic detection of a Schiff's Base, taking as examples the reaction between other amino acids and other aldehydes and ketones.

Reaction (1), which proceeds rapidly in an alkaline medium, has already been used several times for the alkalimetric determination of amino acids [4]. The polarographic method, however, for which, as will be shown below, neither the extent or completeness of reaction (1) toward the right hand side, nor the basicity of the Schiff's Base formed are of any significance, is superior to the alkalimetric method. In addition, the polarographic method can be applied to amino acid concentration which are appreciably lower than those that can be handled by the alkalimetric method.

Polarographic studies were carried out on an ÉP-312 electronic polarograph. The cell, which was fitted with an external reference electrode (saturated calomel electrode), was thermostatted at 25 ± 0.3°. Oxygen was purged with nitrogen. The capillary characteristics taken in 0.1 N H_2SO_4 at a potential of −0.9 v were : for capillary No. 1 $m^{2/3} t^{1/6} = 1.05$ $mg^{2/3} t^{-1/2}$, and for capillary No. 2 $m^{2/3} t^{1/6} = 3.16$ $mg^{2/3} t^{-1/2}$.

The purity of the amino acids used, according to the results of microanalysis, were: ϵ-ACA, 99%; AEA, 95.2%; APA, 94.9%. We were unable to establish the purity of AUA.

The formaldehyde used was technical grade material with an initial concentration of 32% CH_2O; its concentration was established iodometrically [6].

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* S. P. Grishaeva took part in the experimental work.

Buffer solutions were prepared from Na_2HPO_4 and citric acid.

A clearly defined wave (Fig. 1) corresponding to a Schiff's Base could be observed within a few minutes of adding formaldehyde to an alkaline solution (NaOH) of the amino acids. The wave height does not change with time. This indicates that reaction 1 reaches an equilibrium state rapidly, in agreement with the results of alkalimetric studies [4]. As pointed out already, the wave is located at potentials which are more positive than that of formaldehyde. Thus, for ε-ACA, $E_{1/2} = -1.30$ v in 0.1 N NaOH, while under the same conditions $E_{1/2}$ for formaldehyde is −1.59 v [7].

Thus it should be possible to carry out a polarographic determination of amino acids in alkaline solution after addition of formaldehyde. In an alkaline solution of 0.1 N NaOH, however, the constant of the limiting current is very low. In buffer solutions at pH 6-8, and in acid solutions at pH 1-2, the wave is 5-8 times greater than in 0.1 N NaOH. Taking this fact into account, we carried out most of our experiments in 0.1 N H_2SO_4 (the wave form shown in Fig. 1). In all these experiments reaction (1) was carried out in about 0.2N NaOH, after which the solution was neutralized and 0.1 N H_2SO_4 or buffer solution added. Since it was necessary to neutralize 0.2 N NaOH, and in the case of caprolactam also necessary to neutralize about 1 N H_2SO_4, the solution being polarographed also contained 0.1-0.25 N Na_2SO_4.

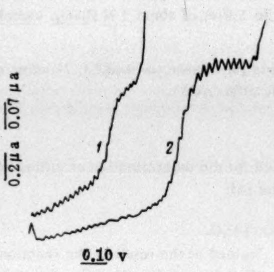

Fig. 1. Polarograms of the Schiff's Base from ε-ACA: $C_{AA} = 0.885$ mM/liter; $C_F = 1.6\%$. 1) 0.1 N NaOH; 2) 0.1 N H_2SO_4 + 0.25 N Na_2SO_4.

TABLE 1. Limiting Current Constants ($\dot{i}_k$) and Half-Wave Potentials ($E_{1/2}$) for the Schiff's Bases from Amino Acids (Capillary No. 1)

Acid / i_k, $E_{1/2}$	ε-ACA	AEA	APA	AUA
$\dot{i}_k \frac{\mu a}{mM}$	0,357	0,400	0,490	0,707
$--E_{1/2}$	0,81	0,79	0,75	0,70

It was established that the wave height increases with increasing formaldehyde concentration. Accordingly, while studying the relationship between the limiting current and amino acid concentration, the formaldehyde concentration of the solution being polarographed was kept constant at 3.8%; in the alkaline solution in which reaction (1) was carried out the formaldehyde concentration was 6.1%. Although an increase in formaldehyde concentration increases the wave height, and thereby the sensitivity of the method, it is not desirable to increase the formaldehyde concentration in the solution being polarographed beyond 4-5%, since formalin often contains impurities which lead to some increase in the current in the region of the Schiff's Base wave. Bearing this in mind, in cases where the amino acid concentration is very low (hundredths of mM/liter) the supporting electrolyte should be checked polarographically.

For eliminating maxima which are only observed at high amino acid concentrations (> 5-10 mM/liter) 0.02% gelatin solution was added.

There is a linear relationship between the limiting current and amino acid concentration over a fairly wide range (Fig. 2): for ε-ACA from 0.038 to 35.0 mM/liter; for AEA from 0.033 to 26.2 mM/liter; for APA from 0.055 to 16.5 mM/liter; and for AUA from 0.049 to 0.49 mM/liter.

Table 1 contains the limiting current constants and the corresponding half-wave potentials, which are almost independent of the amino acid concentration. As the results in the table show, the further the amino group from the carboxyl group the greater is the shift in the half-wave potential toward the positive side, and the greater the limiting current constant.

Using the calibration curves $i_k - C_{AA}$, a large number of determinations of amino acids in solution were carried out (Table 2). The accuracy is not less than ± 3% (relative).

TABLE 2. Polarographic Determination of Caprolactam in Solution

Taken, mM/liter · 10^2	Found, mM/liter · 10^2	Error, % (relative)	Taken, mM/liter	Found, mM/liter	Error, % (relative)
9,20	9,98	—2,4	0,860	0,880	+2,3
7,25	7,15	—1,4	0,750	0,755	+0,6
10,2	10,4	+2,2	0,916	0,935	+1,6
11,9	12,2	+2,2	0,962	0,975	+1,3
6,72	6,59	—2,2	0,892	0,915	+2,6
8,14	8,35	+2,7	0,883	0,895	+1,4
11,7	11,4	—2,6	0,930	0,915	—1,6
12,9	12,6	—2,3	1,10	1,12	+1,3
8,95	9,15	+2,2	1,01	1,03	+2,0
14,6	14,5	—0,7	1,40	1,36	—2,9

TABLE 3. The Relationship Between the Limiting Current of the Schiff's Base from ϵ-ACA and the Height (h) of the Mercury Reservoir, and Formaldehyde Concentration (C_F) in the Solution Being Polarographed (without gelatin). C_{AA} = 0.885 mM/liter (Capillary No. 2).

C_F, %	h, cm			
	30	40	50	60
0,032	A 0,568	0,568	0,575	0,582
	B 0,104	0,0897	0,0813	0,0752
0,32	A 0,764	0,781	0,781	0,800
	B 0,139	0,122	0,111	0,103
3,2	A 1,16	1,20	1,27	1,33
	B 0,212	0,189	0,179	0,171
6,4	A 1,49	1,67	1,74	1,85
	B 0,272	0,264	0,246	0,238
12,8	A 1,93	2,11	2,25	2,36
	B 0,352	0,334	0,318	0,304
19,1	A 2,04	2,18	2,32	2,47
	B 0,372	0,344	0,328	0,319
25,5	A 2,14	2,25	2,44	2,51
	B 0,391	0,356	0,345	0,324

Note: A = i_k, μa; B = $i_k/\sqrt{h}$, μa·cm$^{-\frac{1}{2}}$

RESULTS

There is no direct relationship between the limiting current and the square root of the height of the mercury reservoir; this indicates that the limiting current is kinetic in character. The kinetic character of the limiting current (Tables 3,4) is maintained on increasing the formaldehyde concentration, and also at varying pH.

The results obtained enable one to advance some hypotheses regarding the mechanism of the development of the polarographic wave of a Schiff's Base.

As noted already, in an alkaline medium reaction (1) finishes by rapid establishment of an equilibrium with an equilibrium constant $K'_{\text{equilib.}}$ In an acid medium of 0.1 N H_2SO_4, presumably because of the conversion of the amino group into $\overset{+}{N}H_3$, a Schiff's Base is not in general formed; this also explains the absence of a wave on adding formaldehyde directly to an acid solution.

On the basis of [8] we assume that only nonhydrated formaldehyde participates in the reaction with the amino group. Taking into account the equilibrium

$$CH_2O + H_2O \overset{K''_{\text{equilib.}}}{\rightleftarrows} CH_2(OH)_2, \tag{2}$$

TABLE 4. Effect of pH of the Buffered Supporting Electrolyte (withoud gelatin) and the Height (h) of the Mercury Reservoir on the Polarographic Characteristics of the Schiff's Base from ϵ-ACA; C_{AA} = 0.885 mM/liter; C_F = 1.6% (Capillary No. 2) 1) h, cm.

h, cm	30		40		50		60		$-\varphi_{1/2}$
pH	A	B	A	B	A	B	A	B	
1,0*	0,93	0,170	0,97	0,153	0,98	0,139	1,00	0,129	0,75
2,2	0,87	0,159	0,93	0,147	0.97	0,137	1,00	0,129	0,75
3,1	0,49	0,0898	0,53	0,0840	0,57	0,0805	0,58	0,0750	0,76
3,6	0,37	0,0677	0,40	0,0633	0,44	0,0622	0,44	0,0569	0,80
5,2	0,58	0,106	0,60	0,0950	0,62	0,0876	0,64	0,0826	0,89
6,2	0,75	0,137	0,78	0,123	0,82	0,116	0,86	0,111	0,92
6,7	1,13	0,206	1,13	0,179	1,17	0,165	1,17	0,151	0,94
7,3	1,46	0,267	1,43	0,226	1,50	0,212	1,54	0,199	0,98
7,8	1,65	0,302	1,65	0,261	1,72	0,243	1,72	0,222	1,01
8,2	—	—	—	—	—	—	1,58	—	1,07
9,5	1,12	0,205	1,16	0,183	1,20	0,170	1,25	0,161	1,09
13,0**		—	—	—	—	—	0,19	—	1,30

Note: A = i_k, μa; B = $i_k/\sqrt{h}$, $\mu\text{a}\cdot\text{cm}^{-\frac{1}{2}}$.

*0.1 N H_2SO_4.

**0.1 N NaOH.

and also that the total formaledehyde concentration (C_F) is very much greater than the total concentration of amino acid (C_{AA}), the concentration of the Schiff's Base (C_{SB}) can be expressed by:

$$C_{SB} = \frac{K_{\text{equilib.}} C_{AA} \cdot C_F}{1 + K_{\text{equilib.}} \cdot C_F} \tag{3}$$

where

$$K_{\text{equilib.}} = K'_{\text{equilib.}} \frac{1}{K''_{\text{equilib.}} + 1}\,. \tag{4}$$

As indicated already, the polarographic wave of the Schiff's Base has a kinetic character. This is explained by the fact that the chemical reaction proceeds on the electrode surface. The nature of this reaction has not yet been explained.

Assuming the monomolecularity of the limiting stage of the electrode process with respect to the Schiff's Base, we obtain on the basis of the theory of kinetic currents [9,10]:

$$i_k = a\mu_1 k_1 C^S_{SB}$$

$$k_d (C_{SB} - C^S_{SB}) = a\mu_1 k_1 C^S_{SB}\,. \tag{5}$$

$$a = nFq \cdot 10^{-3} \tag{6}$$

where i_k is the limiting current; q is the mean surface of the mercury drop; n is the number of electrons in the electrode reaction; μ_1 is the thickness of the reaction layer; C^S_{SB} is the concentration of the Schiff's Base on the electrode surface; k_1 is the velocity constant of the limiting chemical stage of the electrode process; and k_d is the diffusion current constant of the Schiff's Base.

Solving equation (4), (5), and (6) simultaneously, we obtain:

$$i_k = \frac{K_{\text{equilib}} \cdot k_d \cdot C_{AA} \cdot C_F}{\left(1 + \frac{k_d}{a\mu_1 k_1}\right) (1 + K_{\text{equilib}} \cdot C_F)}\,. \tag{7}$$

It follows from equation (7) that at C_F = const, and for a given height (h) of the mercury reservoir, there should be a linear relation between the limiting current and the amino acid concentration; as we have already seen this is confirmed experimentally.

Thus, amino acids can be determined polarographically even when the yield of a Schiff's Base by reaction (1) is considerably less than 100%. It is assumed of course that the equilibrium of reaction (1) in 0.1 N H_2SO_4 is not shifted during the life of a mercury drop [8]. Moreover, as will be shown below, it can be assumed that after rapid neutralization and acidification of the alkaline solution, the equilibrium of reaction (1) will be "frozen."

Since $\frac{k_d}{\sqrt{h}}$ is independent of h, then the equation $i_k = f(h, C_F)$ at C_{AA} = const will assume the form:

$$i_k = \frac{A\sqrt{h}\cdot C_F}{(1+B\sqrt{h})(1+K_{equilib.}C_F)}, \tag{8}$$

where

$$A = K_{equilib.}\cdot\frac{k_d}{\sqrt{h}}\cdot C_{AA}, \tag{9}$$

$$B = \frac{k_d}{\sqrt{h}\, a\mu_1 k_1}. \tag{10}$$

In the case of ϵ-aminocaproic acid, equation (8) is in good agreement with experimental results over a fairly wide formaldehyde concentration range, and for appreciable changes in the height of the mercury reservoir (Table 5). The following values were found in this case: A = 120, B = 1.2, and $K_{equilib.}$ = 103. Calculations showed that equation (7) is in considerably better agreement with experimental data if the formaldehyde concentration in the alkaline medium (0.2 N NaOH) is taken into account rather than its concentration in the solutions being polarographed (0.1 N H_2SO_4). The formaldehyde concentration given in Table 5 correspond to those in alkaline solutions. This result indicates that the equilibrium in reaction (1) is "frozen" after neutralization and acidification of the alkaline solution. A similar phenomenon could be predicted from [8], which shows that the velocity constants of the forward and reverse reactions of urea with formaldehyde are sharply depressed on shifting the pH to the acid region.

TABLE 5. Comparison of Experimental and Calculated Limiting Currents for the Schiff's Base from ϵ-ACA; C_{AA} = 0.885 mM/liter (Capillary No. 2)

h, cm	30		40		50		60	
	i_k, μa							
C_F, mM/liter	measured	calculated	measured	calculated	measured	calculated	measured	calculated
$1,75\cdot10^{-2}$	0,54	0,54	0,57	0,55	0,58	0,56	0,58	0,56
$2,42\cdot10^{-2}$	0,61	0,60	0,61	0,61	0,61	0,62	0,63	0,63
$3,00\cdot10^{-2}$	0,63	0,64	0,63	0,65	0,64	0,66	0,64	0,66
$3,51\cdot10^{-2}$	0,66	0,66	0,68	0,67	0,69	0,68	0,68	0,69
$9,52\cdot10^{-2}$	0,73	0,77	0,75	0,78	0,73	0,79	0,75	0,80
0,137	0,77	0,79	0,77	0,80	0,77	0,81	0,78	0,82
0,175	0,77	0,80	0,77	0,81	0,77	0,82	0,79	0,83
0,300	0,82	0,82	0,84	0,83	0,84	0,84	0,88	0,85
0,952	0,93	0,83	0,97	0,85	0,98	0,86	1.00	0,87

It follws from equation (7) that at high values of C_F (C_F > 1 M), i_k should not depend on C_F. It has been shown experimentally, however, that the growth of i_k with increase in C_F continues even when C_F is considerably greater than 1 M (Table 3). It is possible that this can be explained by the partial influence at high formaldehyde concentrations of the reaction between amino acid and hydrated formaldehyde (which is polymerized to some extent at C_F > 1 M).

It is of interest to note that the values of A=120 and $K_{equilib.}$=103 are in good agreement with equation (9).

if one assumes the reaction to be a two-electron process, and the diffusion coefficient of the Schiff's Base from ϵ-aminocaproic acid is calculated from the mobility of the caproate anion [11]. Presumably, therefore, reduction proceeds across the double bond with formation of methylaminocaproic acid. There is a published reference [12] to the reduction of the Schiff Base CH_2NCH_2COOH by hydrogen in an acid medium to methylaminoacetic acid CH_3NHCH_2COOH.

From the value of $K_{equilib.} = 103$ it is possible to calculate $K'_{equilib.}$, the equilibrium constant for process (1), in the case of the interaction of ϵ-aminocaproic acid with formaldehyde in 0.2 N NaOH. For this purpose we calculated $K_{equilib.} = 1.4$ (process II) on the basis of the results given in [8] (0.05 N LiOH, 25°). Substituting $K_{equilib.} = 103$ and $K''_{equilib.} = 1.4$ in equation (4) we found that $K_{equilib.} = 250$. This value indicates that even in a 1 M formaldehyde solution the yield of a Schiff's Base is almost 100%. The increase in yield of a Schiff's Base from glycine with increasing formaldehyde concentration was noted in [13]. Determination of the value of the equilibrium constant of process (1) is of great importance for the practical application of the alkalimetric method of determining amino acids.

It was pointed out above that the limiting current constant (see Table 1) is greater the further the amino group is removed from the carboxyl group in the amino acid molecule. Since under these conditions in reaction (1), the formaldehyde concentration was sufficiently high (about 6%), and bearing in mind that for ϵ-ACA, $K_{equilib.} = 103$, the reason for the growth of i_k must be the increase in the velocity constant of the limiting chemical stage in the series: ϵ-ACA, AEA, APA, and AUA. Since the basicity of the nitrogen in this series increases, one cannot exclude the possibility that the limiting stage is the addition of a proton on the nitrogen atom.

The relation between i_k and pH (see Table 4), which could throw light on the limiting chemical state of the electrode reaction, was a very complex one. Over the pH range 1-2, $i_k = \text{const}$; subsequently i_k drops with increasing pH. At pH > 4, i_k starts to increase, while at pH > 8 there is a sharp drop in i_k. Presumably, such a complicated character of the i_k — pH relationship can be explained by the simultaneous effect of pH in different directions: both on equilibrium (1) (at pH's close to 7 and greater than 7) and on the kinetics of the electrode process.

Finally we should like to point out that the possibilities of the polarographic detection of Schiff's Bases may be widely used in the chemistry of polymers, including the analysis of proteins.

SUMMARY

Methods have been developed for the polarographic determination of caprolactam in the form of ϵ-aminocaproic acid, and also for the determination of other amino acids by their rapid conversion (0.2 N NaOH) into polarographically active Schiff's Bases (reaction with formaldehyde) which give one clearly defined wave at all pH values of the supporting electrolyte. This wave occurs at potentials which are more positive than that of the formaldehyde wave.

A linear relationship has been established between the limiting current and total amino acid concentration (0.1 N H_2SO_4). The limiting current constant increases in the series ϵ-aminocaproic acid; 7-aminoenathic acid; 9-aminopelarogonic acid; 11-aminoundecanoic acid. The half-wave potentials are shifted to more positive values in the same succession; the limiting current is kinetic in character.

On the basis of data obtained during a polarographic study of the Schiff's Base obtained from ϵ-aminocaproic acid, a quantitative evaluation has been made of the effect of formaldehyde concentration and the height of the mercury reservoir on the value of the limiting current. The equilibrium constant of the reaction between ϵ-aminocaproic acid and formaldehyde has been determined.

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BRIEF COMMUNICATIONS

PURIFICATION OF CERTAIN QUATERNARY AMMONIUM COMPOUNDS USED IN POLAROGRAPHY

G. S. Supin

Scientific Research Institute of the Tire Industry, Moscow

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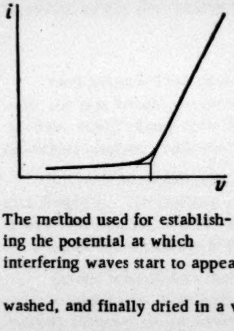
Tetraalkylammonium compounds used as supporting electrolytes in polarography have to meet very strict purity requirements. These compounds should be purified even from trace amounts of impurities which give polarographic waves or catalytically depress the hydrogen overvoltage on a dropping mercury cathode. Večék [1] has suggested difficult and complicated methods of purifying tetramethylammonium chloride and iodide by repeated crystallization from alcoholic solution using the tetramethylammonium base obtained by means of silver oxide. Another method [2] of purifying tetramethylammonium chloride by means of methanol and acetone can only be carried out by using completely anhydrous solvents. A method has also been published for purifying tetrabutylammonium iodide [3].

In the work described here the extent to which the quaternary ammonium salts have been purified was assessed polarographically on the basis of the potential value (relative to the saturated calomel electrode) at which interfering waves start to appear in a 0.1 N aqueous solution of the test material, the potential being determined graphically (see figure). Numerous experiments showed that the potential value determined in this way is independent of the chosen sesnsitivity of the galvanometer and can characterize the purifity of the solution. An LP-55 polarograph was used at a sensitivity of S = 1/10 – 1/100; the dropping period of the capillary was 6 sec at zero applied potential.



The method used for establishing the potential at which interfering waves start to appear.

Contact between the solution and a saturated calomel electrode was established via an electrolytic bridge 1/3 filled with a 2% gel of agar-agar prepared in a 0.2 N aqueous solution of $(C_2H_5)_4NI$, and 2/3 filled with saturated KCl solution. At high galvanometer sensitivities oxygen was purged from solution with nitrogen.

Many quaternary ammonium salts are very readily soluble in water [$(CH_3)_4NI$ is sparingly soluble], so that recrystallization from aqueous solutions is usually complicated because of the low yield of purified product. Accordingly, purification techniques were developed in which two organic solvents were used, the two solvents chosen being such that the purified material is readily soluble in one of them and sparingly soluble in the other (Table 1). Using such a technique it was found possible to purify three of the quaternary salts studied in similar fashion, the only difference being the nature of the solvents used. According to this technique, 10 g of the salt to be purified is dissolved in the solvent indicated; the solution is filtered and a precipitant added to the filtrate; the precipitate is collected on a filter, washed, and finally dried in a vacuum desiccator. Results are given in Table 2.

The solubility of tetramethylammonium iodide increases sharply with rising temperature [4]; the salt can be purified by recrystallization from water in this way. Thirty g of $(CH_3)_4NI$ is dissolved in 100 ml water on boiling; the hot solution is filtered; and the crystals which separate out on cooling are filtered off from the mother liquor, washed with cold water, and dried. The salt is then redissolved in 100 ml of boiling water and poured into a glass beaker contained in a large vessel containing water heated to 100°, after which it is left overnight for slow cooling. The crystals which separate out are filtered off, washed, and dried. The yield is 50%. The mother liquors can be evaporated down to recover the salt. When the method described was used, starting with a salt for which the potential at which interfering waves started to appear was –2.05 v, a product was obtained for which the corresponding potential was –2.3 v; this product is suitable for the polarographic determination of potassium and sodium.

A more careful purification can be carried out by prolonged extraction of tetramethylammonium iodide with chloroform. For this purpose the salt which has been purified by recrystallization from water is dried, ground, and

TABLE 1. Solubility of Tetraalkylammonium Salts in Water and in Some Organic Solvents

Test material	Water	Methanol	Ethanol	Acetone	Ethyl ether	Chloroform
Tetramethylammonium chloride $(CH_3)_4NCl$	Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble
Tetramethylammonium bromide $(CH_3)_4NBr$ *	55 (15°)		Sparingly soluble	■		■
Tetramethylammonium iodide $(CH_3)_4NI$	4.2 (20°) 43 (95°)	0.5 (20°) 1.0 (60°)	0.025	■	■	■
Tetraethylammonium chloride $(C_2H_5)_4NCl$	141 (25°)	Soluble	Soluble	Soluble		Soluble
Tetraethylammonium bromide $(C_2H_5)_4NBr$	Soluble	■	■	■	Soluble	■
Tetraethylammonium iodide $(C_2H_5)_4NI$	45 (25°)	■	2.9 (27°)	Insoluble	Insoluble	0.87 (20°)

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* Thevalues quoted refer to the solubility in g per 100 g of solvent. Results for $(CH_3)_4NBr$ and $(C_2H_5)_4NCl$ are taken from Dictionary of Organic Compounds, 1949, IL, Moscow, pp. 689 and 721.

TABLE 2. Purification of Tetralkylammonium Salts

Material to be purified	Solvent	Precipitant	Washed on the filter with:	Yield, %	Potential at which interfering waves start to appear, v (relative to the saturated calomel electrode)	
					Original material	Purified material
Tetramethylammonium chloride	Mixture of 50 ml methanol and 100 ml chloroform	200 ml ether	50 ml ether	75	−2.3	−2.6
Tetraethylammonium bromide	50 ml chloroform	100 ml benzene	50 ml benzene	80	−2.2	−2.8
Tetraethylammonium iodide	Mixture of 5 ml methanol and 100 ml chloform	50 ml benzene	50 ml ether	65	−2.35	−2.75

100 ml of chloroform added to it. After extraction for 7-10 days with periodic stirring, the salt is transferred to a filter, washed with 50 ml of chloform, dried, and recrystallized from water on slow cooling. Chloroform treatment can be replaced by a water extraction (300 ml of water) over a period of one month.

In aqueous solutions of a salt purified in this way the potential at which the hydrogen wave starts to appear is −2.65 v. Recrystallization of $(CH_3)_4NI$ from methanol does not give satisfactory results.

SUMMARY

New methods have been developed for purifying tetramethylammonium chloride and iodide, and tetraethylammonium bromide and iodide. The purified products can be used for polarographic determinations in extremely negative potential regions.

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THE INCREASE IN THE SENSITIVITY OF THE POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF VANADIUM AND PHOSPHATE IONS

V. G. Sochevanov, N. V. Shmakova, L. T. Martynova,
and G. A. Volkova

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Starik et al.[1] and later Sinyakova [2] and other research workers have pointed out the considerable influence which vanadium compounds exert on the polarographic reduction current of UO_2^{2+}. The nature of this phenomenon was first studied and explained by Sochevanov and Shmakova in 1953, and was subsequently confirmed by Morachevskii and Sakharov [3].

When the vanadium content of the solution is unknown, quantitative polarographic determination of uranium is impossible. When, on the other hand, the vanadium concentration of the solution is established at a constant level, this has a beneficial effect on the determination of uranium, because of an increase in the polarographic current of uranium to ten times and more, and because of the increased sensitivity of determination.

During polarographic determination of uranium in synthetic solutions containing vanadium, it was established that good results can be obtained in a chloride medium which is 0.5 M with respect to HCl and 1 M with respect to chloride ions. The vanadium can be conveniently introduced into solution in the form of a concentrated solution of sodium vanadate.

A solution which has a constant concentration relative to H^+ and Cl^- is prepared by adding 2 ml of concentrated HCl to a known volume of a standard solution of uranyl chloride contained in a 25-ml standard flask, and then adding a known volume of sodium vanadate solution. The orange colored solution is reduced on heating to 40-50° with the minimum amount of ascorbic acid. Completion of reduction is readily observable by the appearance of a pure blue color. To the solution obtained in this way is added 0.6 ml of 10 M NaOH and 10 drops of 0.1% thymol solution, after which the volume is made up to the mark with water and the whole thoroughly mixed. After an aliquot of the solution has been purged with hydrogen or CO_2, it is polarographed over the polarization voltage range 0.0-0.4 v (saturated calomel electrode).

Polarographic waves for uranium before and after addition of vanadium are compared in Fig. 1. Figure 2 shows the relation between the wave height for the reduction of uranium and the concentration of quadrivalent vanadium in solution. It is clear from these curves that vanadium strongly affects the wave height of uranium.

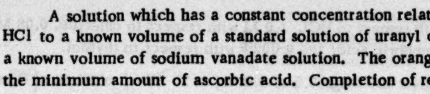

Fig. 1. Effect of vanadium on the polarographic wave of uranium when the concentration of the latter is 10^{-4} M. Vanadium concentration, M: 1) 0; 2) 4×10^{-2}; 3) 5.6×10^{-2}; 4) 8.0×10^{-2} M UO_2^{2+}.

At high vanadium concentrations, oscillations increase and the uranium wave starts to fuse with the wave for the reduction of the trivalent vanadium ions formed.

Phosphoric acid is added to the solution to improve the upper section of the uranium wave and to eliminate the wave of trivalent vanadium; phosphoric acid depresses the uranium wave to some extent, but it depresses or leads to the complete disappearance of the trivalent vanadium wave (Fig. 3 and table).

The linear nature of the relationship between the uranium wave height and phosphoric acid concentration

Phosphoric acid concentration, M · 10^4	Uranium wave ht. h		$h_0 - h_x$	$\frac{h_0 - h_x}{c} \cdot 10^{-4}$
	mm	%		
0,00	25,0	100	—	—
2,21	24,0	95,0	5,0	2,26
4,42	22,8	91,2	8,8	1,98
6,63	21,2	84,9	15,1	2,28
8,84	20,3	81,2	18,8	2,13
11,05	19,0	76,0	24,0	2,17
14,47	16,5	66,0	34,0	2,35
		Mean		$2,21 \cdot 10^{-4}$

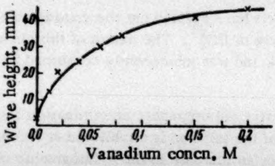

Fig. 2. The relationship between uranium wave-height and the vanadium concentration of the solution

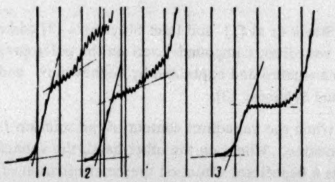

Fig. 3. Effect of phosphoric acid on the wave height of uranium when the concentration of the latter is 10^{-4}M, in the presence of vanadium at a concentration of 8×10^{-2}M. H_3PO_4 concentration, M: 1) 0.0; 2) 0.2×10^{-3}; 3) 1.11×10^{-3}.

indicates that it could be used for an indirect polarographic determination.

Uranium is determined polarographically in a supporting electrolyte of the following composition: 0.5 M with respect to HCl, 1.0 M with respect to chloride, 0.08 M with respect to vanadium, 1.0×10^{-3}M with respect to phosphoric acid, and 0.002% with respect to thymol.

The wave height is proportional to uranium content over the range 0.0 to 2.0 mg in 25 ml of solution, or from 0.0 to 3.36×10^{-4}M.

Fe^{III}, Pb, Cu, etc., which usually interfere, should be removed beforehand during determination of uranium in complex mixtures. For example, good results are obtained by precipitating ammonium diuranate from a complexon-containing solution on a column packed with silica gel [4].

SUMMARY

It has been found that the shape of the polarographic wave of uranium, which is catalyzed by quadrivalent vanadium ions, improves in the presence of phosphate ions.

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PHOTOMETRIC DETERMINATION OF CERIUM

A. I. Cherkesov and T. S. Zhigalkina
Saratov State Teaching Institute and the Astrakhan Technical Institute
of the Fish Industry and Economy
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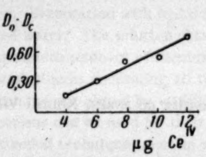
Photometric methods are used for the determination of small amounts of cerium in minerals and cerium-containing alloys; these methods include: the peroxide [1], benzidene [2], 8-hydroxyquinoline [3], citrate [4], o-tolidine [5], etc., photometric methods. We have developed a rapid photometric method for the determination of small amounts of cerium, which does not involve separating if from a number of accompanying elements; the method is based on the oxidation – reduction interaction between quadrivalent cerium and the halochromic compound of an azo dye with sulfuric acid [6].

Of a number of azo dyes tested for this purpose, methyl orange and methyl red proved to be the most suitable.

The methyl orange solution should be prepared in 60% H_2SO_4, while the methyl red solution should be prepared in 80% H_2SO_4; the absorption maximum of the first solution occurs at 496 mμ, while that of the second lies at 533 mμ. Both dyes give almost identical results; accordingly, we shall only give the results obtained when methyl red was used.

With addition of increasing amounts of quadrivalent cerium salts to a sulfuric acid solution of methyl red, the optical density of the dye solution decreases. When the difference D_0-D_C is plotted along the ordinate and the cerium concentration (in μg / ml) plotted along the abscissa, a curve in the form of an ascending straight line is obtained (figure).



This relation is expressed mathematically by the equation for a straight line $D_0-D_C = KC$, where D_0 is the optical density of the dye solution (free from cerium), D_C is the optical density of the dye solution after addition of C μg cerium per ml of solution, and K is the proportionality coefficient.

Preparation of Solutions for Constructing a Calibration Curve. 0.0202 g of $Ce(SO_4)_2 \cdot 4H_2O$ is dissolved in 2 N H_2SO_4 in a 250-ml standard flask; 1 ml of this solution contains 28 μg of cerium. A 10^{-4} - $3 \cdot 10^{-4}$M solution of methyl red is prepared by dissolving the reagent in an 80% by volume aqueous solution of chemically pure sulfuric acid; if the sulfuric acid contains appreciable amounts of oxidizing impurities it should be treated with a 0.05 N $KMnO_4$ solution (the first drops are immediately decolorized on mixing; the treatment is stopped when the rose color persists for 3-5 sec).

Three ml of dye solution is introduced into each of 6 test tubes; to the first test tube is added 1 ml of the cerium salt solution, while 1.5 ml is added to the second, 2.0 ml to the third and so on; 4 ml of 2 N H_2SO_4 is added to the sixth test tube; the volumes of the solutions in test tubes 1-5 are also made up to 7 ml with 2 N H_2SO_4. The solutions are mixed and the optical density measured after 10-15 min.

The optical densities obtained D_0 (sixth test tube) and D_C, and C (μg) are given in the table (see Table 1). A calibration curve is constructed within the coordinates D_0-D_C and C on the basis of these results.

TABLE 1. Data for Construction of a Calibration Curve

D_0	D_0	D_0-D_c	C, μg Ce^{IV}/ml
2,00	1,85	0,15	4
	1,70	0,30	6
	1,55	0,45	8
	1,35	0,65	10
	1,20	0,80	12

In order to determine the cerium content of the test solution 1 ml of this solution is added to 3 ml of dye solution; the volume is made up to 7 ml with 2 N H_2SO_4 and the solution mixed; its optical density D_C is measured after 10-15 min, and the difference D_0-D_C determined; on the basis of this difference, and using the calibration curve, the cerium content in μg corresponding to each ml in the final volume (7 ml) is established.

Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, MoO_4^{2-}, UO_2^{2+}, Cu^{2+}, and Co^{2+} in amounts of 1000 μg per 6 μg of cerium do not interfere with cerium determination; neither do Fe^{3+}, Cl^-, and NO_3^- interfere as long as not more than 50-100 μg of each of these ions is present per 6 μg of cerium.

Results for the determination of cerium in the presence of all the ions listed above are given in Table 2.

TABLE 2. Determination of Cerium in the Presence of Other Ions (6.0 μg Ce taken)

Me added, μg	Ce^{IV} found, μg	Deviation, μg
Cu^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+} MoO_4^{2-}, UO_2^{2+} 1000 μg of each Fe^{3+}, Cl^-, NO_3^- 100 μg of each	6,5; 5,5; 6,5 6,0; 6,2; 6,5 6,2; 5,5; 6,0	0,5; 0,5; 0,5 0,0; 0,2; 0,5 0,2; 0,5; 0,0

SUMMARY

A photometric method is suggested for the determination of small amounts of cerium by means of a sulfuric acid solution of methyl red; the method is based on the oxidation– reduction reaction of the azo dye with quadrivalent cerium. The decrease in the optical density of the azo dye solution is linearly related to the amount of cerium added to the solution.

Moderate amounts of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+}, MoO_4^{2-}, UO_2^{2+}, Cl^-, and NO_3^- do not interfere with cerium determination.

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DETERMINATION OF RHENIUM IN ALLOYS

D. I. Ryabchikov and A. I. Lazarev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Small amounts of rhenium in alloys can be determined photometrically by the thiocyanate method [1]; ions which possess an intrinsic color or which form sparingly soluble or colored compounds interfere in this method. Copper ions form a sparingly soluble thiocyanate. We have succeeded in determining rhenium in solutions containing not more than $8 \cdot 10^{-5}$ g-ion copper/liter. Thiourea complexes copper into a colorless complex and permits determination of rhenium in the presence of $2 \cdot 10^{-3}$ g-ion copper/ liter. At high thiourea concentrations a rhenium thiourea complex is formed which has different properties than the thiocyanate compound [2].

For determination of rhenium in alloys by the thiocyanate method we separated rhenium from the other components beforehand by ion exchange chromatography. Rhenium is not held back by cation exchange resins and passes into the filtrate; the cations remain on the ion-exchange column [3,4]. The cations which remain on the column can be subjected to subsequent separation or can be eluted completely into solution. Nitrates, which interfere with rhenium determination, are removed by a double evaporation of the solution with hydrochloric acid.

An iron-based alloy containing large amounts of aluminum, manganese, nickel, and up to 15% copper was analyzed. 0.1 g of alloy is dissolved in 10 ml of an acid mixture consisting of 5 ml of hydrochlorid acid (1 : 2) and 5 ml of nitric acid (1 : 1). Solution is effected on gentle heating, and the solution is evaporated to a volume of 0.5-1 ml on a water bath. Evaporation should be carried out carefully since rhenium compounds are volatile from acid solutions. To the residual solution is added 5 ml of concentrated hydrochloric acid and the evaporation is repeated. Evaporation with hydrochloric acid is repeated once again. The salts are dissolved on stirring in 50 ml of distilled water. The solution obtained is passed through an ion-exchange column at a rate not exceeding 4 ml/ min. For complete removal of rhenium anions it is sufficient to wash the column with 150 ml of water. The filtrate and wash liquors containing all the rhenium are collected in a 250-ml standard flask. The cations remaining on the column are eluted by washing the column with 200 ml of 4 N sulfuric acid. The acid solution containing all the cations can be used for their determination. Separation of rhenium from the other alloy components by the recommended technique takes up to 50 min.

A 50-ml buret containing 10 g of the cation exchange resin KU-2 serves as the ion-exchange column. The resin is kept in position in the buret with a plug of glass wool. The cation exchange resin is converted into the $H^{\cdot}$ form by successive washing of the column with 100 ml of 2 N hydrochloric acid and 100 ml of distilled water.

The rhenium solution in the standard flask is made up to the mark with distilled water. 5-10 ml of this solution is transferred to a 50-ml standard flask; 20 ml of hydrochloric acid (1 : 1) is added, followed by 2 ml of a 50% potassium thiocyanate solution and 2 ml of a 20% solution of $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid, and the volume made up to the mark with distilled water. The solution is mixed after addition of each reagent. The optical density is measured after 10 min in a FÉK-M photoelectrocolorimeter fitted with a blue filter; distilled water is used as the reference. The rhenium content is determined by means of a calibration curve constructed with the aid of pure potassium perrhenate.

The standard solution is prepared by dissolving 0.1554 g of potassium perrhenate in 100 ml of 1 N hydrochloric acid; 1 ml of this solution contains 1 mg of rhenium. Solutions of the requisite concentration are obtained by diluting this standard solution.

Direct photometric determination with thiourea [2] was studied as a possible way of speeding up and simplifying the determination of rhenium in alloys. In acid solutions in the presence of a reducing agent, thiourea forms with rhenium compounds a complex compound which has a greenish color. The maximum absorption of the complex lies in the short-wavelength region of the spectrum. The relation between optical density and concentration is linear over a wide concentration range (5-160 μg Re in 25 ml). The molar extinction coefficient of the rhenium thiourea complex is $6.2 \cdot 10^3$.

Formation of the thiourea complex is slow at room temperature. Dissolution of the alloy and evaporation of the nitric acid are carried out as decribed in the previous instance. Fifty ml of distilled water is added to the evaporated solution, and mixing carried out until the salts dissolve. The contents of the beaker used are transferred to a 200-ml standard flask and the volume made up to the mark with distilled water. A 25-ml aliquot of the solution is transferred to a 50-ml standard flask; 10 ml of concentrated hydrochloric acid is added and the solution cooled; 10 ml of a 5% aqueous solution of thiourea is added; this is followed by 2 ml of 20% $SnCl_2 \cdot 2H_2O$ solution, and the volume finally made up to the mark with water. Optical density is measured using a light filter with maximum transmission at 400 mμ.

Results of Rhenium Determination

Wt. of alloy, g	Rhenium found, %	
	by the thiourea method	by the thiocyanate method after chromatographic separation
0,103	0,58	0,60
0,113	0,64	0,61
0,120	0,60	0,59
0,133	0,61	0,61
0,144	0,65	0,62
0,161	0,61	0,62

Results of rhenium determination by the two recommended methods are given in the table.

SUMMARY

Small amounts of Re in alloys can be determined by the thiocyanate method after preliminary separation of rhenium by means of a cation exchange resin.

Direct photometric determination of rhenium as its thiourea complex is more rapid.

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SEPARATION OF IRON FROM COBALT BY MEANS OF CUPFERRON DURING SOIL ANALYSIS

L. T. Ikramov
Tashkent Pharmaceutical Institute
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Cobalt cupferronate is readily extracted from an aqueous layer by chloroform at pH about 2, while iron cupferronate is extracted quantitatively by the same solvent at pH <1. The technique for separating iron from cobalt reduces to the following. Hydrochloric acid is added to the test solution contained in a separation funnel until the acid concentration is approximately 1 M; the volume of the solution should be 10-15 ml. Seven ml of a 6% aqueous solution of cupferron is then added in the cold; the solution is mixed and is then shaken up with 10 ml of chloroform. The chloroform layer, which has a red color from the iron cupferronate, is discarded; 3 ml of cupferron solution is added, followed by 5-7 ml of chloroform. Extraction with chloroform in the presence of cupferron is repeated until the chloroform layer has a yellow color.

The aqueous phase is evaporated to dryness on a water bath. If the dry residue has a yellow color because of the presence of cupferron, the latter is destroyed with a mixture of nitric acid and hydrogen peroxide (3 : 1) with addition of a few drops of sulfuric acid.

To determine the cobalt, the solution obtained is evaporated to dryness on a water bath. The residue is dissolved in 10 ml of a mixture of 0.5 ml of concentrated hydrochloric acid, 0.5 ml of concentrated nitric acid and 9 ml of water. The solution, which is heated to the boil, is mixed with 5 ml of a 50% sodium acetate solution and 2 ml of a 0.1% solution of nitro-R-salt, and the whole boiled for not less than one minute. Two ml of concentrated HNO_3 is added to the mixture obtained and the whole boiled again for one minute. The red colored solution is diluted to a known volume and the color of the final solution compared visually in a colorimeter tube with a scale prepared beforehand.

TABLE 1. Determination of Cobalt after Removal of Iron with Cupferron

Taken		Ratio between $Co^{2+}:Fe^{3+}$	Co^{2+} found		Taken		Ratio between $Co^{2+}:Fe^{3+}$	Co^{2+} found	
Co^{2+}, μg	Fe^{3+}, mg		μg	%	Co^{2+}, μg	Fe^{3+}, mg		μg	%
10	10	1 : 1000	9,5	95	30	20	1 : 666	29,5	98,2
15	30	1 : 2000	14,5	96,5	40	60	1 : 1500	39	97,5
20	10	1 : 500	19	95	50	30	1 : 600	48,5	97
25	50	1 : 2000	24	96	50	50	1 : 1000	49	98
30	10	1 : 333	29	96 57					

As the results given in Table 1 show, determination of cobalt after removal of iron by means of cupferron gives completely satisfactory results.

Determination of cobalt in soils gave encouraging results. For this purpose varying amounts of iron and cobalt salts were added to an aliquot of soil (5 g). The soil was calcined in a porcelain crucible in a muffle at a weak red heat for 1.5-2 hr. The crucible was cooled and 10 ml of concentrated HCl and 10 ml of concentrated HNO_3 added. The solution was evaporated to dryness on a water bath. The residue was dissolved in 20 ml of 1 M hydrochloric acid and filtered. The filtrate was transferred to a separating funnel and the iron removed by means of cupferron as described above.

TABLE 2. Determination of Cobalt in Soil (5 g) after Removal of Iron

Added		Co^{2+} found		Added		Co^{2+} found	
Co^{2+}, µg	Fe^{3+}, mg	µg	%	Co^{2+}, µg	Fe^{3+}, mg	µg	%
—	—	15,0		20	5	34,0	95,0
—	—	14,5		23	8	36,5	93,48
—	1	15,3		25	9	40,0	100,0
15	2	29,5	96,66	30	10	44,0	96,66
18	3	32,0	94,44				

Table 2 shows that cobalt is removed from iron quantitatively by means of cupferron, and is determined reasonably accurately.

SUMMARY

A technique has been developed for separating iron from small amounts of cobalt by extracting the former as its cupferronate with chloroform. The method has been checked by determining cobalt in soils; good results were obtained.

THE PHOTOMETRIC DETERMINATION OF ACETIC ACID IN THE PRESENCE OF OTHER ACIDS

Yu. P. Artsybasheva and I. A. Favorskaya

A. A. Zhdanov Leningrad State University

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Of the numerous methods of determining acetic acid [1] the photometric method is the most selective. The method is based on the capacity of basic lanthanum acetate to give a color with iodine. Kruger and Tschirch [2] suggested this reaction for the qualitative detection of acetate ions; Cl^-, PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Mg^{2+} and organic materials which reduced iodine interfere. It was subsequently found that lactic and pyruvic acids also interfere. Propionic acid, like acetic acid, gives a blue color. Under certain conditions the reaction mentioned can be used for the quantitative determination of acetic acid [3,4]. Hutchens and Kass [4] have determined microamounts of acetic acid in the media used for the culture of microorganisms. After removal of interfering inorganic materials, acetic acid can be determined with an accuracy of 3-5%. Fluoroacetic acid and other halogen-substituted acetic acids can be determined with the same accuracy.

In the work described here we used the method indicated for the rapid quantitative determination of acetic acid without removing it beforehand from the mixture of acids. We were interested in the possibility of determining acetic acid quantitatively in the products from the ozonolysis of vinyl acetylene hydrocarbons, i.e., in the presence of formic, trimethylacetic, and trimethylpyruvic acids, the concentrations of which corresponded to their content in the ozonolysis products.

As we established, trimethylpyruvic acid, like pyruvic acid, interferes with the determination by reducing iodine. Nevertheless, after oxidizing the trimethylpyruvic acid and distilling off the acetic acid by the method suggested below, the acetic acid can be determined with an error of 1-3%.

EXPERIMENTAL

Preparation of Solutions. 0.02 N aqueous iodine solution (2.54 g of chemically pure iodine and 33.2 g of chemically pure potassium iodide are dissolved in one liter of distilled water); 2.5% lanthanum nitrate solution [12.5 g of chemically pure $La(NO_3)_2$ in 500 ml distilled water].

Formic acid : commercial product.

Trimethylacetic acid (m.p. 34°) was synthesized from tertiary butyl chloride and carbon dioxide by Grignard's method.

Trimethylpyruvic acid (m.p. 90-91°) was prepared by oxidation of pinacoline with permanganate [5].

We used a calibration curve which was constructed using a solution of sodium acetate obtained by titrating an accurately weighed amount of acetic acid with 0.1 N NaOH.

All optical density measurements were carried out on a FÉK-N-54 apparatus using a No. 8 filter (transmission maximum at 656 $m\mu$).

Experimental Procedure. One ml of solution containing 0.08-0.25 mg of acetate was introduced into a 5-6 ml test tube with a well-fitting ground stopper. One ml of 2.5% lanthanum nitrate was carefully added along the test tube walls, and this was followed by 0.1 ml of 0.02 N iodine solution and finally by 1 ml of 0.1 N ammonia solution. The contents of the test tube were heated for 5 min on a boiling water bath, and were then cooled in a beaker of water and the optical density of the solution measured after 30 min in a cuvette with l = 1 cm. A control solution was prepared in parallel and the optical density of the colored solutions measured relative to it. It should be emphasized that the order in which the reagents are added must be strictly adhered to. Hutchens and Kass in their paper [4] recommend that a "combined" reagent be prepared by mixing equal volumes of ammonia and lathanum nitrate and adding 2 ml of the mixture obtained to the acetate solution. According to our observations, under these conditions the color only develops after standing for a long time or not at all. This can be explained by the fact that the basic lanthanum acetate originally formed and which is not capable of adsorbing iodine reacts very slowly with acetate. At very low acetate concentrations the color only develops after heating and has a slightly greenish tinge.

When trimethylpyruvic acid and acetic acid were present simultaneously, the acetic acid was determined after oxidation of the keto acid with chromic mixture. Twenty-five ml of solution containing a known amount of acetic and trimethylpyruvic acids, 0.5 g of potassium dichromate, and 1 ml of concentrated sulfuric acid were introduced into a 250-ml Kjeldahl flask fitted with a dropping funnel, a Kjeldahl adapter and a condenser. The mixture was heated for one hour to the boil. The acid products obtained were steam distilled and 0.1 N NaOH added until the pH was 8.2-10 as measured by a pH meter. The volume of the neutralized distillate was made up to 250 ml and the acetic acid determined as described above.

Determination of Acetic Acid in the Presence of Other Acids

Amount of acetic acid, mg		Error		Ratio of the concentration of formic (I), trimethylacetic (II), and trimethylpyruvic (III) acids to acetic acid concentration		
taken	found	mg	%	I	II	III
29,50	29,21	0,29	0,98	—	—	—
11,79	11,52	0,27	1,29	—	—	—
23,60	22,71	0,89	3,77	10	—	—
17,71	17,36	0,35	1,97	10	—	—
29,50	29,32	0,18	0,61	—	8	—
23,60	23,12	0,48	2,03	—	11	—
73,87	73,75	0,12	0,16	—	—	5
21,94	21,63	0,31	1,41	—	—	10
29,50	29,12	0,38	1,28	5	10	3
23,60	23,46	0,14	0,59	10	10	10

It is clear from the table that formic and trimethylacetic acids do not interfere with the determination, even when their concentration is ten times that of acetic acid. The error of the method described for determination of acetic acid is 1-3%.

SUMMARY

It has been established that it is possible to determine acetic acid photometrically in mixtures containing large amounts of formic and trimethylacetic acids. Acetic acid can only be determined in the presence of trimethylpyruvic acid when the latter has been oxidized beforehand.

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QUANTITATIVE DETERMINATION OF MONOFUNCTIONAL ALCOHOLS BY MEANS OF ACRYLONITRILE

S. I. Obtemperanskaya, A. P. Terent'ev, and M. M. Buzlanova

M. V. Lomonosov Moscow State University

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We showed in a previous paper [1] that acrylonitrile is a suitable reagent for the quantitative determination of thioalcohols and thiophenols. The reaction between acrylonitrile, thioalcohols, and thiophenols proceeds quentitatively in the absence of a catalyst. Further work on studies of the possibility of using acrylonitrile in organic analysis has shown that this reagent can be used for the quantitative determination of alcohols when the reation is carried out in an alkaline medium. Acrylonitrile reacts with alcohols according to the equation $ROH + CH_2 = CH \cdot CN \rightarrow ROCH_2CH_2CN$ [2].

By adding a known excess of acrylonitrile dissolved in dioxane to the reaction mixture and determining the excess of the reagent by the sulfite method we suggested earlier [3,4], it is possible to determine primary and secondary alcohols, and alcohols with certain other functional groups, quantitatively. In the cases of polyfunctional alcohols (ethylene glycol) only one of the hydroxyl groups reacts quantitatively in the cold. For primary alcohols the reaction is complete after 1hr to 1hr 30 min at room temperature, and 15-30 min at 35-40°; the reaction takes 3-6 hr at room temperature and 1 hour to 30 min at 35-40° in the case of secondary alcohols. An essential prerequisite is that the dioxane and acrylonitrile be carefully purified from peroxides and other impurities. Water interferes with the determination since it reacts with acrylonitrile in the presence of alkali.

The acrylonitrile is shaken with a sodium hydroxide solution; it is then dried first with potash, then with magnesium sulfate, and finally distilled. Dioxane is boiled under reflux for several hours with finely cut sodium metal and then distilled over sodium.

Results of determinations of alcohols are given in the table.

Experimental Procedure. About 1 mM of test alcohol is introduced into a 25-ml standard flask; 5 ml of dioxane is added, followed by 0.02-0.03 g of finely group potassium hydroxide. The flask is stoppered and carefully shaken until the alkali has dissolved completely, after which dioxane is added to the mark. One ml of the solution prepared is introduced into a ground-neck conical flask; 2 ml of 1 N acrylonitrile solution is added (72 g acrylonitrile in one liter of dioxane); the flask is stoppered and allowed to stand (for primary alcohols, 1 hour to 1 hr 30 min at room temperature or for 15-30 min at 35-40°; for secondary alcohols, 3-6 hr at room temperature, or for 1 hr to 1 hr 30 min at 35-40°).

After the reaction is complete, excess acrylonitrile is determined: 25 ml of 1 M sodium sulfite (240 g of the septihydrate in one liter of boiled distilled water) is added to the flask; this is followed by 5-7 drops of mixed thymolphthalein-alizarin yellow indicator (the indicator is prepared by mixing 30 ml of a 0.1% alcoholic solution of thymolphthalein with 15 ml of 0.1% aqueous alizarin yellow solution) and the liberated alkali titrated with 0.1 N hydrochloric acid until the blue color disappears and a yellow color appears.

A blank test is carried out simultaneously. Two ml of acrylonitrile is added to 25 ml of sulfite solution, and after 5 min, 1 ml of the prepared solution of test alcohol added. The solution is finally titrated with 0.1 N acid, using the same indicator.

Results are calculated by means of the formula

$$\% \, OH = \frac{(a - b) \, N \cdot 17}{c \cdot 10},$$

where a and b are the number of ml of acid used for titrating the blank and the test solution respectively; c is the weight of alcohol taken; and N is the normality of the acid.

Test material	Time	Temperature, °C	% OH	
			Found	Calculated
Methanol	45 min	Room	53.10	53.06
	1 hr	"	52.98	
	20 min	30-35	53.10	
	20 min	30-35	53.04	
Ethanol	1 hr 45 min	Room	36.88	36.90
	1 hr 45 min	"	36.99	
n-Propanol	1 hr	"	28.25	28.29
	1 hr 45 min	"	28.32	
n-Butanol	1 hr 30 min	"	22.92	22.94
	1 hr 30 min	"	22.95	
	15 min	45	22.92	
	20 min	45	22.95	
n-Amyl alcohol	40 min	Room	19.28	19.28
	40 min	"	19.20	
n-Heptyl alcohol	1 hr 20 min	"	14.62	14.63
	1 hr 20 min	"	14.57	
	35 min	35-40	14.62	
	35 min	35-40	14.67	
Allyl alcohol	1 hr	Room	29.32	29.27
	1 hr	"	29.19	
Benzyl alcohol	15 min	"	15.71	15.73
	25 min	"	15.76	
Isobutanol	40 min	"	22.98	22.97
	40 min	"	22.88	
Isoamyl alcohol	40 min	"	19.29	19.28
			19.35	
Cyclohexylcarbinol	30 min	"	14.91	14.89
	30 min	"	14.88	
Phenyl ethyl alcohol	30 min	"	13.93	13.91
	30 min	"	13.85	
Phenyl propyl alcohol	30 min	"	12.54	12.48
			12.48	
Isopropanol	45 min	"	28.32	28.29
	5 hr 30 min	"	28.32	
Cyclohexanol	2 hr 30 min	"	17.02	16.97
	2 hr 30 min	"	16.98	
	1 hr	35-40	16.93	
	1 hr	35-40	16.93	
Secondary butanol	1 hr	35-40	22.97	22.97
	1 hr	35-40	22.83	
Heptanol-4	1 hr 30 min	35-40	14.63	14.63
			14.60	
Ethylene cyanhydrin	3 hr	Room	23.91	23.92
			23.93	
Ethyl cellosolve	30 min	"	18.85	18.87
$CH_2(OH)CH_2(OC_2H_5)$	30 min	"	18.87	

SUMMARY

A titrimetric method has been developed for the determination of primary and secondary alcohols, using their reaction with acrylonitrile in the presence of alkali.

The reaction takes some tens of minutes (at 35-40°).

The reaction is carried out in dioxane solution. The excess acrylonitrile is determined by the sulfite method.

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ANALYSIS OF BINARY MIXTURES OF TETRACHLOROALKANES

K. I. Sakodynskii and N. N. Umnik

L. Ya. Karpov Scientific Research Physicochemical Institute, Moscow

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Analysis of mixtures of tetrachloroalkanes (TCA) obtained by telomerization of carbon tetrachloride with ethylene is a difficult problem. Thus, despite appreciable differences in the boiling points, during analysis of mixtures of TCA by analytical distillation on a fractional distillation column, a high degree of accuracy is not obtained. Moreover, a comparatively large amount of sample is required when this technique is used. Gas liquid chromatography would appear to be the most promising method for analysis of mixtures of TCA.

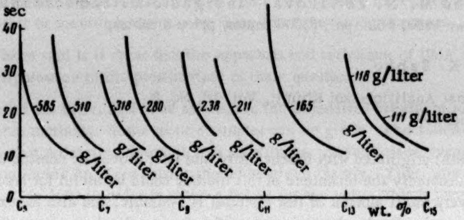
During studies of the distribution of adjacent TCA between different solvents during extraction, and determination of the partition coefficients of binary mixtures during evaporation, it is necessary to carry out a series of express analyses of binary mixtures of TCA. In such a case the simple and fairly accurate method of analysis developed in detail for the determination of the isotopic composition of water [1] is very convenient to use. The method is based on measuring the dropping time of drops of the test samples in a viscous medium. The dropping time is proportional to the density, which depends on the composition of binary mixtures of components with different densities. The density of the medium in which the drops are allowed to fall should be similar to that of the test samples in order that the dropping time is long enough for it to be measured. Since individual TCA have different densities, and the density difference amounts to 0.09 for C_5-C_7 mixtures and 0.02 for C_{15}-C_{17} mixtures, it is impossible to choose one medium which is suitable for the determination of the dropping time for all binary mixtures of TCA [2]. The most suitable media for measuring the dropping rate of drops of binary mixtures of TCA were found to be aqueous solutions of $Na_2S_2O_3$ for C_5-C_7 mixtures and NaCl solutions for C_7-C_{15} mixtures. Chemically pure reagents were used for preparing the requisite solutions, the NaCl concentration being subsequently determined argentimetrically and the $Na_2S_2O_3$ concentration iodometrically.

Calibration curves were constructed with the aid of standard mixtures of TCA, and the latter were prepared by weighing out aliquots of individual TCA; microburets were used for measuring out the aliquots so that the compositions of the mixtures differ from each other by approximately 10%. Pure, individual TCA obtained by a double distillation on a ladder-type laboratory column used for molecular distillation [13] were used for preparing the standard mixtures. In order to measure out drops of exactly the same size, a capillary of the type used for isotopic analysis of water was used. The test tube holding the solution had a diameter of 10 mm and was about 35 cm long. The test tube was immersed in a thermostat kept at 25 ± 0.1°. The thermostat temperature does not have to be controlled accurately because aqueous solutions are used. The dropping time was determined by measuring the time taken by a drop to pass two marks 15 cm apart. The dropping time was determined 10-12 times, results differing by more than ± 0.3 sec from the mean value as a result of random deviations in the size of the drops being rejected. Before measurement the mixtures were shaken, since it was found that on standing there was a tendency to fractionate according to density.

Since it was found that a medium with one density was insufficient for determination of the concentration of even one binary system with the requisite degree of accuracy, the concentration range measured was divided into two sub-ranges which overlapped. Solutions of the following concentrations were used: for C_5-C_7 mixtures, 585 and 510 g $Na_2S_2O_3$/liter; for C_7-C_9, 318 and 280 g NaCl/liter; for C_9-C_{11}, 238 and 211 g NaCl/liter; for C_{13}-C_{15}, 118 and 111 g NaCl/liter; and for C_{11}-C_{13}, 165 g NaCl/liter. The calibration curves for the binary mixtures are shown in the figure.

When the calibration curves have been constructed, analysis reduces to determination of the mean dropping time. A check carried out on control samples showed that the method ensures an accuracy of ± 0.5-1% absolute, the accuracy being higher the greater the dropping time.

The method developed for the analysis of the composition of binary mixtures of TCA is rapid and gives results which are accurate enough. By introducing some improvements (using a longer measuring tube, and subdividing the concentration range into a larger number of subdivisions) it should be possible to enhance the accuracy of the method, should this be necessary.



Calibration curves for binary mixtures of TCA.

SUMMARY

A method for the analysis of binary mixtures of tetrachloroalkanes has been developed which is based on measuring the dropping time of test mixtures in a viscous medium. Dropping time is a function of density which depends on the composition of a binary mixture.

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Reviewed by A. K. Babko

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Ultramicroanalysis (UMA) originated with biochemistry and later proved of considerable help in the development of radiochemistry. Undoubtedly the technique of this method could be useful for analytical chemistry, mainly in those cases where only a very small amount of test material is available, and also for examining analytical concentrates of microimpurities. Accordingly, the appearance of a short textbook on inorganic UMA in which a description is given of the basic techniques and possibilities of the method is very timely.

At the very beginning the authors emphasize that their aim is to describe the techniques and apparatus of UMA using known chemical and physicochemical methods. In UMA, concentration sensitivity remains almost the same as in macromethods; the absolute amount of test material can be reduced a thousand, tens of thousands, and hundreds of thousands times.

For working on the microscale, special apparatus and vessels are required,which the research worker often has to make himself. Of special importance is the large increase in relative surface. The basic apparatus—microscope, micromanipulators, piston attachments for micropipets, humidity cabinets, and some other apparatuses— are described very briefly, in about ten pages.

A large part of the book is devoted to questions of qualitative UMA. A description is given of the general technique for observing the formation of colored compounds, and individual techniques are also considered. From the tables included, it is clear, e.g., that when the thiocyanate reactionfor iron is carried out on the macro scale the limit of identification is 10^{-5} g, while using UMA it is possible to detect 10^{-9} g. It should be pointed out that the authors at this juncture depart from their undoubtedly correct assertion that the concentration sensitivity depends on the physicochemical properties of the material formed, and not on the scale of the experiment. It follows from Table 6 that though the concentration sensitivity for the detection ofiron by UMA increases ten times, the sensitivity of the detection of chromium increases by more than ten times. It must be assumed that in this case the authors are using insufficiently critically checked results, and one has to believe what the authors have written in the text.

The technique of observing certain precipitation reactions is described. The main techniques are described briefly but usually clearly enough. Some instructions are however incomprehensible. For example,it is difficult to imagine what is meant by the following:"... the cone plus precipitate are placed in a capillary fused at both ends and containing a drop of water. "

In addition to the usual techniques of forming colored compounds, and of precipitation reactions, more than half the book is devoted to less well known UMA techniques such as deposition of metals by electrolysis, chromatographic methods, extraction with organic solvents from volumes of 10^{-3} - 10^{-5} ml, etc. Qualitative UMA of certain materials is described; the use of Russian-made apparatus for taking micro samples is interesting.

Only about one third of the book is devoted to quantitative UMA. In this section, in addition to the usual methods of gravimetric and titrimetric analysis, the use of electrochemical methods of titration, as well as of colorimetry and spectrophotometry, is discussed. It seems, despite what the authors say, that the impression is created that titrimetric UMA is a very difficult method. Naturally, the change-over from the usual scale of qualitative or gravimetric analysis to the UMA scale also requires some skill on the part of the analyst. Nevertheless, the experimental technique often reduces to carrying out simple operations by micromanipulators. The use of potentiometric and amperometric methods of titration in UMA would appear to be rather pointless. Thus,if any particular material can be titrated amperometrically this means that it could also be determined polarographically. Essentially, amperometric titration was developed with the aim of decreasing the sensitivity of polarography (the accuracy being increased at the same time). If, then, one is seeking for ways of determining ultrasmall amounts, the use of amperometric titration cannot be regarded as the right approach; polarographic determination of microvolumes is considerably simpler than amperometric titration.

A more favorable impression is gained on reading the last section of the book, which is devoted to descriptions of colorimetric and spectrophotometric UMA methods. Here one has only to replace the usual cuvette by a microcuvette, the usual colorimeter or spectrophotometer by some other measuring apparatus, and this is easily done in practice.

From all that has been said it is clear that the apparatus and technique of UMA are presented widely, and the reader can gain a clear impression of the present state of these questions.

Among the defects of the book, indicated above, are the unjustified brevity of some sections, and insufficiently critical evaluation of some methods. Some more examples can be given. The authors are quite correct in some instances where they say that a detailed description is superfluous. Nevertheless, even in a short book, if it has been decided that a description should be given then it should be given clearly. Thus, why (and how?) "split a thick-walled capillary in two ..."(p.122) in order to make a holder for the vessel. This is incomprehensible.

In conclusion the authors give a short but interesting paragraph on the possible development of inorganic UMA. One cannot but agree with the views advanced here. Nevertheless, there should be some discussion of some supplementary problems. At least two other possible lines of approach can be mentioned which would help the development and extension of the application of UMA.

a) The use of sparingly volatile organic solvents. Difficulties associated with the rapid evaporation of micro drops of aqueous solutions are dealt with several times in the book under review. The difficulties are even greater when nonaqueous solutions are used; extraction requires special conditions and becomes extremely awkward. In UMA, however, many of these difficulties could be overcome by using such solvents as glycerol, nitrobenzene, supercooled salol and other solvents. At the same time the study of chemical reactions in such solvents would supplement our over-all chemical understanding.

b) One of the most valuable applications of UMA, as pointed out in the book, would be its use for the determination of microimpurities. Obviously, in such cases, the work would have to start with macrosamples and an analytical concentrate of the microimpurities prepared. The concentrate should then be analyzed by UMA. Taking into account the characteristic features of UMA, the conclusion can be drawn that the most valuable technique for the preparation of analytical concentrates would probably be the method of organic coprecipitants suggested by V. I. Kuznetsov; were such a technique used after combustion, the ultramicro amount of test impurity thus obtained directly could then be analyzed by UMA. Such methods, however, have not as yet been developed.

On the whole, the book under review is of undoubted interest and enriches our literature on analytical chemistry.

A. Okac, "Qualitative analytische Chemie"
Akademische Verlagsgesellschaft, Leipzig, 1960. 644 pp.

Reviewed by I. N. Marov

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3,
pp. 378-379, May-June, 1961

This book was first published in 1956 in Prague in Czech, and it was published in German by the Leipzig Academic Press in 1960. In this edition a number of chapters in the book have been expanded appreciably, and it includes a new chapter on physical methods in analytical chemistry. The appearance of a new edition of the book is to be welcomed since there has long been a need for a modern textbook on qualitative analysis.

The book contains some brief information on the history of analytical chemistry and the development of qualitative chemical analysis; the most important theoretical questions relating to qualitative analysis, the technique of carrying out qualitative and microcrystalloscopic reactions are discussed, etc. A number of new group and selective reactions are described in addition to the classical group reactions.

Sodium carbonate, acetate, and phosphate, potassium chromate, hydrochloric and sulfuric acids,etc.,are used as group reagents as well as organic materials (hydroxyquinoline, anthranilic acid, dithizone, cupferron, etc.).

A considerable part of the book (300 pages out of 640) is devoted to selective reactions. This section is very rich in material on selective reactions for almost all elements. A number of such reactions are given for each element, and, as a rule, possibilities are indicated of direct establishement of the presence or absence of a particular element in test samples.

The last chapter, which is devoted to a review of some physical methods used in analytical chemistry, should in the author's opinion serve as a short textbook, by means of which a chemist should be able to choose the method he wants. One of the best features of the book is the vast bibliography (945 references) given at the end of the book. It covers the literature up to 1958.

Okač's book has taken into account modern achievements in theory and practice and is a valuable textbook on qualitative analysis for students in chemical faculties and for analytical specialists.

Houben-Weyl, "Methoden der organischen Chemie"

Reviewed by V. G. Tiptsova

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3,
p. 379, May-June, 1961

Methoden der organischen Chemie (Houben-Weyl). Vierte völlig neu gestaltete Auflage. Herausgegeben von E. Müller. Unter besonderer Mitwirkung von O. Bayer, H. Meerwein, K. Ziegler. Verlag G. Thieme, Stuttgart.

Bd. 1/2. Allgemeine Laboratoriumspraxis. Teil 2. Bearbeitet von A. Berthmann, K. Blumrich, W. Büche, W. Bunge, R. Jaecker, H. Jonas, ... 1959, 1017 pp.

Bd. V/4. Halogenverbindungen. Brom- und Jodverbindungen — Herstellung. Chlor-, Brom- und Jodverbindungen —Reaktivität, Umwandlung. Bearbeitet von N. Kreutzkamp, H. Meerwein, A. Roedig, R. Stroh, 1960, 894 pp.

Bd XI/2. Stickstoffverbindungen II. und III. Bearbeitet von H. Bestian, L. Birkhofer, A. Dorlars, H. Freytag, ... 1958, 840 pp.

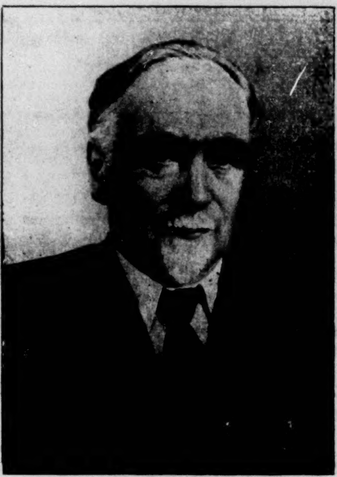
The second part of the first volume of Houben-Weyl's reference work is devoted to general laboratory methods. Among the various questions which are examined in detail are modern methods of preparing, purifying drying, and storing gases, while the technique of working with liquefied gases in an inert gas atmosphere and the technique of working with small amounts of material at low pressure are described. The properties and purification of the most important organic solvents are discussed, as well as drying techniques.

The fourth part of the fifth volume is devoted to a detailed review of methods of preparing bromine- and iodine-containing compounds, and to the various transformations of organic compounds of chlorine, bromine, and iodine. The second part of the eleventh volume is devoted to the various transformations of amines, 1,2- and 1,3-alkyleneamines, amino acids, and lactams. There is a wealth of information on quaternary ammonium bases and on compounds containing nitrogen and sulfur.

The volumes of Houben-Weyl under review, like those published earlier [see Zhurnal analit. khimii 13, 376 (1958)], contain a very large bibliography and the well-compiled index is set out extremely well.

The new edition of this fundamental reference work of Houben-Weyl with its wealth of valuable material is of great interest not only for analytical chemists working on synthesis and studying new organic reagents but also for organic analytical chemists. The material on general laboratory methods is valuable for a wide circle of chemical research workers.

OBITUARY



YURII VITAL'EVICH MORACHEVSKII

Soviet chemical science suffered a heavy loss on January 4, 1960. On that date Professor Yurii Vital'evich Morachevskii died; he was outstanding in the field of analytical chemistry, geochemistry, and halurgy, he was head of the chair of analytical chemistry at Leningrad State University and of the analytical laboratory of the Institute of Silicate Chemistry, Academy of Sciences, USSR. He was also a member of the Commission on Analytical Chemistry, Academy of Sciences, USSR and a doctor of chemical sciences.

The scientific research work of Morachevskii is distinguished by its exceptional breadth and variety, although it was concentrated on problems relating to an all-round study of mineral raw materials. His scientific activity was closely connected with the solution of important practical problems in the social economy. During his life Morachevskii combined his scientific research with a large amount of teaching and organizational activity.

Morachevskii was born on July 11, 1894. He finished at Leningrad university in 1917 and started to work at the All-Union Geological Institute (Geological Committee) as an analytical chemist, and later became a scientific group leader and head of the geochemical section. During the middle twenties, with the turbulent growth of geological prospecting work in the USSR, the chemical laboratory of the Geological Institute under the direction of Morachevskii also expanded– from a group consisting of a few analysts to a large scientific reasearch establishment including eight special laboratories and about 150 co-workers. At the same time, Morachevskii was responsible for organizing dozens of laboratory field parties, instructing analytical chemists, and personally conducting experimental work developing new methods of analyzing many types of mineral raw material. Yu. V. Morachevskii was one of the fundamental organizers of chemical service in geology.

Morachevskii initiated the publication and was the chief editor and author of many sections of the reference work "Analysis of Mineral Raw Material," in which the experience of many analytical chemists was collected. The second edition of this work, considerably revised and supplemented, was brought out in 1956 under the editorship of Morachevskii and Yu. N. Knipovich.

Morachevskii, as a geochemist, was widely known for his studies of salt deposits of the Soviet Union. His most important works, "Features of the Geochemistry of the Verkhnekamsk Salt Deposits," "Conditions for the Formation of Deposits in the Solikamsk Lagoon," "Gas-Bearing of Potassium Salts of the Verkhnekamsk Deposits," and a number of others, are parts of a single, broadly developed work dealing thoroughly and for the first time with the geochemistry of the Solikamsk Deposit of potassium salts, the largest in the world.

One must include the huge amount of work which Morachevskii carried out, and the help he gave in connection with exploring and planning the construction of the Solikamsk Hydro Projects and a number of other large hydrotechnical constructions.

In the course of his work in the Leningrad Mining Institute (1936-1941) Morachevskii carried out important research on the copper-nickel ores of the Trans-Polar region, their geochemistry, the distribution of accompanying elements in them, and their behavior during metallurgical processing.

With his wide knowledge and huge experience Morachevskii was closely connected with the many Institutes in Leningrad and other cities.

For many years Morachevskii led a very fruitful teaching career. From 1944 he was head of the school of analytical chemists at Leningrad University and contributed immensely to the education of young scientists. Morachevskii reorganized the teaching of analytical chemistry in Leningrad University, organized a course on the theoretical bases of analytical chemistry and the analytical chemistry of the rare elements, and introduced a number of new specialist courses and practical work to the chair. Morachevskii tried to educate analysts with a broad outlook, possessing a knowledge of the basic methods of modern analytical chemistry.

The main subject at the chair of analytical chemistry was the analytical chemistry of mineral raw materials, particularly questions relating to the analytical chemistry of rare and scattered elements. This naturally encompased a wide range of analytical methods, and Morachevskii saw that it would provide rich training for young analytical chemists. He gave a lot of attention, particularly during the last years of his life, to methods of teaching analytical chemistry, to a correct definition of the problems of analytical chemistry as a science, and to the possibilities of its further development.

In 1950 Morachevskii organized the analytical laboratory in the Institute of Silicate Chemistry, Academy of Sciences, USSR. During the first years of the existence of the laboratory the work carried out was devoted to individual problems relating to the determination of the main components of silicates. In later years, under the direction of Morachevskii, the laboratory moved on to a research plan which he had worked out for developing and improving methods for determining microamounts of various elements in silicates and in elemental silicon.

Spectrochemical methods of determining a number of microimpurities in specially purified material — silica and semiconducting silicon — which were developed under the direction of Morachevskii are distinguished by their high sensitivity. Recently, work has started under Morachevskii's direction on the radioactivation determination of impurities in specially purified silica. To solve these problems, on the initiative of Moracheveskii, a well equipped laboratory of spectrochemical analysis and radioactive isotopes has been set up in the Institute of Silicate Chemistry.

As a member and vice-chairman Morachevskii has contributed largely to the organization and work of the D. I. Mendeleev All-Union Chemical Society, particularly in his own Leningrad Branch. He has lectured often on current problems in chemical science and on the philosophy of natural science.

Despite the poor state of his health, not sparing his strength, he enthusiastically and with deep consciousness of service carried out his numerous duties, right up to the last moment.

The shining image of Yurii Vitalevich, an outstanding scientist, a talented leader and educator of youth, and a charming personality will always stay in the hearts of his numerous pupils and friends.

The Commission on Analytical Chemistry, Academy of Sciences, USSR
Institute of Silicate Chemistry, Academy of Sciences, USSR
A. A. Zhdanov Leningrad State University
Leningrad Branch of the Mendeleev Chemical Society
Editorial Board of "Zhurnal analiticheskoi khimii"

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3,
pp. 380-381, May-June, 1961

EVENTS

PROBLEMS OF MATERIAL (CHEMICAL PHASE) ANALYSIS AT THE CONFERENCE ON METHODS OF ANALYZING SELENIUM-CONTAINING ELEMENTS

B. S. Khristoforov

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3,
pp. 382-383, May-June, 1961

The possibility of establishing the form in which rare and scattered elements occur has hitherto been open to doubt because the chemical properties of these elements have not been studied in sufficient detail, and because of the low concentrations at which they occur. Despite this there has been an increasing number of references published recently on this type of investigation. Nevertheless, the information published on such work is often not complete enough, so that the results of such work cannot be used for developing technological schemes of extracting selenium even during the control of the appropriate processes. In this connection, it is not unimportant that on the initiative of N. S. Greiver and B. V. Dolivo-Dobrovol'skii at a conference held on June 22-27, 1960 at the Leningrad Mining Institute with the purpose of exchanging experience on the application of various methods of determining selenium, tellurium, and the elements which accompany them, a special group of reports and communications was given which dealt with methods of determining the form in which selenium exists in different production materials.

In all, five reports and communications were read at the conference on these questions.

Co-workers at the Central Laboratory of the Leninogorsk Polymetallic Combine V. V. Malakhov, E. D. Glotko, E. I. Savichev, et al., gave a report on the subject "Determination of the Form of Selenium Compounds in Dusts and Distillates from Lead Production."

As the result of studying the elemental composition of dusts from lead production and some products from their processing, as well as the physicochemical conditions for the formation of these products and the values of the heat of formation of different forms of selenium, the authors have suggested that selenium may be present in the dusts and distillates in its elemental form, in the form of its dioxide, and also in the form of the selenates, selenites, and selenides of lead, zinc, mercury, and some other metals. In order to check this assumption, the authors synthesized the compounds listed and studied some of their chemical properties, in particular the action of water on them, and also the action of alkalis, mineral acids, sodium sulfide and sulfite, hydrogen peroxide, and some other reagents.

Comparison of the results obtained enabled the authors to suggest, after a careful check on various production materials, a method for determining the form in which selenium occurs in dusts and distillates from lead production and in certain products obtained during the processing of these materials.

B. S. Khristoforov and R. M. Monasypova (Altai Mining-Metallurgical Scientific Research Institute, Academy of Sciences, Kazakh SSR) in a communication on "The Forms of Selenium in the Sludge from Sulfuric Acid Production at the Ust'-Kamenogorsk Lead-Zinc Combine" showed that it was possible to apply the technique for determining the form in which selenium occurs developed at the Central Laboratory of the Leninogorsk Polymetallic Combine to the study of sulfuric acid sludge from the plant operating on roasting gases from zinc production. It was established that the greater part (up to 70%) of the selenium is present in the sulfuric acid sludges UK STsK in the form of a complex sulfido-selenide of mercury and tin of the type (Hg, Zn) (S, Se) and about 25% in the form of simple lead and zinc selenides.

N. A. Filippova reported on a technique developed at Gintsvetmet for establishing the form in which selenium is present in dusts from lead production.

V. V. Dolivo-Dobrovol'skii and T. N. Greiver (Leningrad Mining Institute) gave a long report on "The Possible Forms of Selenium and Tellurium in Copper Electrolyte Platinum-Containing Sludges"; this report included a detailed description of methods for preparing selenium-containing compounds of silver, palladium, and copper, and also methods and experimental results of a study of the chemical properties of the selenides and selenites of the metals listed. On the basis of the results obtained the authors have developed a technique for determining the content of the enumerated forms in which selenium occurs in the sludges.

Ya. L. Satin and A. P. Meliksetyan (Scientific Research Mining-Metallurgical Institute, Sovnarkhoz Armenian SSR) read a report on "The Determination of Selenium and Tellurium Compounds in the Products from the Sulfating Roasting of Copper Electrolyte Gold-Containing Sludges." They suggested a rational method of analysis which permits determination of selenium dioxide, elemental selenium, tellurium dioxide, silver and copper sulfates, and also the selenides of these metals on one sample.

The participants at the conference listened with interest to reports on development of methods of chemical phase analysis for selenium and tellurium compounds in products from the metallurgical processing of copper-nickel, copper, lead-zinc, and sulfuric acid products. The conference noted the first successes achieved in this field. The hope was expressed that there would be further developments in scientific research work along these directions.

CONFERENCE ON ORGANIC ANALYSIS

Z. I. Podgaiskaya and E. G. Rukhadze

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pp. 383-384, May-June, 1961

The Second All-Union Conference on the Analysis of Organic Compounds was held from April 10-14, 1961 in Moscow; the conference was organized by the Commission on Analytical Chemistry, Academy of Sciences, USSR, the Chemical Faculty of the M. V. Lomonosov Moscow State University, and the Moscow Branch of the D. I. Mendeleev All-Union Chemical Society.

The conference aroused great interest among chemists working on the analysis and synthesis of organic compounds, and also among scientific co-workers, engineers and technicians working in institutes and industrial enterprises with nonchemical interests. The conference was attended by 1000 delegates representing more than 250 scientific research institutes, higher educational establishments, and plant laboratories in 55 cities in the Soviet Union.

The aim of the conference was to gather together the experience of scientific research and practical work in the field of chemical and physico-chemical methods of determining various organic compounds, and to recommend more promising lines of future development with the aim of developing reliable, accurate, and rapid methods. The work of the conference was accordingly divided into eight sections, each section being presided over by leading scientists on their specialist fields, each president giving an introductory general lecture. These reports were devoted to the main achievements in the field of organic analysis in recent years, and to outlining the most promising lines of approach.

N. É. Gel'man and V. A. Klimova read a report on "The Main Lines of the Development of Elemental Microanalysis of Organic Compounds"; A. P. Terent'ev on "Functional Organic Analysis"; L. M. Igonin on "Problems in the Analysis of Monomers and Polymers"; F. M. Shemyakin on "Chromatographic Analysis of Organic Compounds"; A. P. Kreshkov on "New Research on the Analysis of Organic Compounds in Nonaqueous Solution"; É. S. Levin on "The Main Achievements in the Polarography of Organic Materials"; Yu. N. Sheinker on "The Use of Spectroscopy in the Analysis of Organic Compounds"; V. I. Kuznetsov on "Color Reactions and Photometric Methods of Determining Organic Materials"; V. L. Tal'rose, K. I. Zimina, A. A. Polyakova, and G. D. Tantsyrev on "The Mass-Spectrometric Analysis of Mixtures of Organic Materials"; and N. M. Pomerantsev on "The Use of Nuclear Magnetic Resonance in Organic Analysis."

Scientific communications which were given on individual problems at the sessional meetings led to lively discussion. Among these, mention may be made of work on the analysis of silicoorganic compounds by the "wet oxidation method" (A.P. Terent'ev et al.); a titrimetric micromethod of determining sulfur with the new indicator carboxyarsenazo (K.F. Novikova and N. N. Basargin); a new method for the identification of organic compounds by melting points (A. M. Tsukerman); quantitative analysis of epoxide resins by absorption spectroscopy (A. P. Kreshkov et al.); work carried out by N. M. Turkel'taub on the use of gas chromatography for the analysis of hydrocarbon mixtures; analysis of mixtures of organic bases by titration in a methyl ethyl ketone medium (A. P. Kreshkov, N. Sh. Shemet); high frequency titration in organic analysis (V. A. Zarinskii); quantitative analysis of organic compounds by infrared absorption spectra (a number of authors); determination of byproducts from the synthesis of ethylcellulose by means of C^{14} (I. A. Korshunov, M. R. Leonov). Communications on polarographic and mass-spectrometric methods of analysis also evoked considerable interest.

In all more than 130 reports were read and discussed.

It was pointed out in the course of discussion that important successes had been attained in organic analysis. Theoretical studies are being successfully developed. A number of original apparatuses are being made. Modern optical, electrochemical, and chromatographic methods, methods of potentiometric titration in nonaqueous solutions, and also mass spectrometric methods are all being developed. Work is being carried out on the use of nuclear magnetic resonance for the analysis of organic compounds. The accuracy and sensitivity of determinations are increasing.

The conference outlined some measures which will ensure the development and introduction into practice of highly sensitive, accurate, and express methods of analyzing organic compounds, and, in the first instance, methods of analyzing monomeric and polymeric compounds.

The conference turned its attention to the need for a wider development of research on the theory of organic analysis, for a search for new selectively acting reagents and for reactions for identifying organic compounds, including reagents for different functional groups. The need was stressed for the development and introduction into practice of modern chemical, physical, and physicochemical methods of analysis based on the latest instrumental techniques and automation: research must be speeded up.

The conference stressed the necessity of carrying out more research on developing express methods of separating organic compounds (extraction, etc.) and developing methods of microchemical and ultramicrochemical methods of determination, as well as the need for research in the field of natural compounds. The conference also recommended wider use of radioactive indicators.

With the aim of improving the organization and technical quality of work in the analysis of organic compounds, the conference recommended setting up within the system of the Academy of Sciences, USSR and Branch Institutes, Scientific Research Centers, which would organize and coordinate work on the analysis of organic compounds, on the pattern of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, which coordinates work on the analysis of inorganic compounds. At these centers organizing committees whould be set up for constructing and testing new types of apparatuses and equipment. The conference recommended that attention should be given to providing laboratories working on organic analysis with modern apparatus and equipment (chromatographs, semiautomatic and automatic spectrophotometers, potentiometers, high frequency, conductometric, and coulometric setups, etc., in particular, apparatus for high frequency titration made by GEOKhI, Academy of Sciences, USSR, mass-spectrometers, etc),)and also with plenty of different reagents of high quality. The need was also stressed for training analytical chemists specializing in organic analysis.

Particular attention was given to the need for expanding the publication of literature on the analysis of organic compounds; in particular a resolution was adopted that the Praesidium of the Academy of Sciences, USSR, be asked to increase the size of Zhurnal analiticheskoi khimii.

In accordance with the decision of the conference, the Commission on Analytical Chemistry, Academy of Sciences, USSR is at present preparing a monograph, "Analysis of Organic Compounds," for publication.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

THE USE OF MEMBRANE ELECTRODES MADE FROM ION EXCHANGE RESINS FOR POTENTIOMETRIC TITRATION

E. A. Materova and V. S. Yurchenko

A. A. Zhdanov Leningrad State University

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During the last ten years a large number of papers have been published which have been devoted to the electrode properties of membranes made from ion exchange resins. It has been shown in these papers that membranes made from cation exchange or anion exchange resins can funtion as reversible electrodes. Hydrogen and metal functions have been studied in the case of cation exchange membranes [1-10] and also the chloride [11-15], bromide [16], flouride [15] and other functions in the case of anion exchange membranes. The existence of the corresponding electrode functions in the membranes means that the latter can be used in potentiometric titration as indicator electrodes which are, in principle, reversible with respect to any ion e.g. to F^-, NO_3^-, CH_3COO^-, Li^+, Rb^+, Cs^+, Mg^{2+}, Ba^{2+} ions etc, for which no reversible electrodes are known, or preparation of which involves considerable difficulty. In the work described here a study was made of membranes prepared from various Russian resins as indication by the precipitation method.

Many authors have used membrane electrodes for potentiometric titration. Thus Sinkha [17], using electrodes made from IONAK S-200 sulfonated cation exchange resin, and resorcinol-formaldehyde resin, titrated hydrochloric acid with sodium hydroxide, while he used anion exchange electrodes made from the multifunctional anion exchange resin IONAK A-300 and the strongly basic anion exchange resin IRA-400 for some titrations based on precipitation. The curves he obtained did not have a clearly defined potential jump or break at the end point, and it is not clear with what accuracy such a titration can be carried out.

Results of the use of membrane electrodes for potentiometric titration based on precipitation are also given in Parson's article [18]. He used technical Amberplex C-1 cation exchange membranes and anion exchange membranes made from the strongly basic anion exchange resin IRA-400 as membrane electrodes, and titrated sulfuric acid and sodium sulfate with solutions of a barium salt. The authors evaluate the titration error as ± 0.4%.

Fischer and Bancock [19] used electrodes made from inorganic materials for potentiometric titration. Thus they used a membrane made from barium sulfate for titrating sodium sulfate with barium chloride, and for titrating sulfuric acid with barium hydroxide. Sufficiently clearly defined potential changes were not obtained at the end points, however.

Bersier and Trueb [20] used an insoluble film of aluminum oxide for the potentiometric titration of halides. The error in establishing the end point was about 4%.

Experimental Technique. In order to study the behavior of ion exchange electrodes during potentiometric titration, the following ion exchange resins were used: the sulfo-cation exchange resins SBS and KU-2, the carboxyl cation exchange resin KB-4, the resorcinol-formaldehyde resin R, the anion exchange resins EDE-10 and AV-16 substituted to different extents with amino groups, the highly basic anion exchange resin AB-17 containing quaternary ammonium groups, and also the ion exchange membranes DKU-2 (ion exchange resin KU-2 cross-lined with polychlorovinyl).

Susbtitution of the mobile ions in the ionogenic groups of the resins by the requisite ions was carried out by treating the resin with appropriate solutions of acid or salt.

The electrodes were prepared by the technique adopted in the school of physical chemistry of Leningrad State University [7]. In accordance with this method some of the air-dry resin was ground in a ball mill and then sieved. The resin fraction chosen (about 200 mesh) was mixed in a definite proportion by weight with polystyrene dissolved in toluene. The mass while still unsolidified was transferred onto a foil, the toluene removed by evaporation, and the films obtained readily removed from the foil. Ten mm diameter discs were cut out of the films with a drill, the

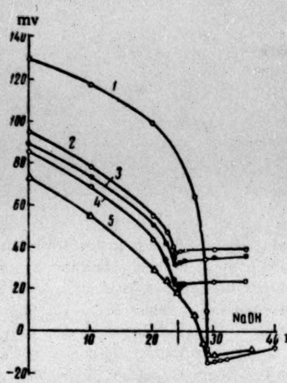

Fig. 1. Titration curves of 1 N hydrochloric acid (25 g) with 0.9572 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), KB-4 (curve 5); titration curves of 0.964 N hydrochloric acid (25 g) with 0·9572 N sodium hydroxide using electrodes made from cation exchange resins SBS (curve 4), SDV-3 (curve 2), and Ku-2 (curve 3).

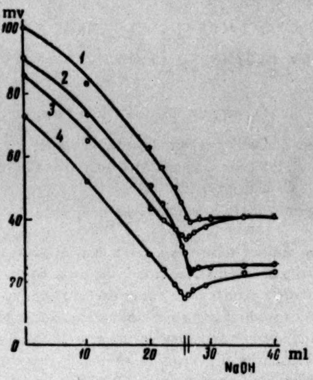

Fig. 2. Titration curves of 1.0858 N nitric acid (25 g) (curves 1 and 2) and of 0.5188 M sulfuric acid (25 g) (curves 3 and 4) with 0.9698 N sodium hydroxide using electrodes made from cation exchange resins SBS (curves 2, 4) and KU-2 (curves 1, 3).

discs were glued with polystyrene glue (a solution of polystyrene in toluene) to polystyrene tubes. The ion exchange resin content of membranes made from the cation exchange resins was 50%, while in the case of membranes made from the anion exchange resins it was 25%.

Before the ion exchange electrodes were used for potentiometric titration, they were calibrated by measuring their potentials in suitable solutions of electrolytes of varying concentration. In these experiments a silver chloride electrode was used as the reference electrode in chloride solutions, and a glass electrode in sulfuric acid solutions. The electrodes chosen were those for which the deviation of the experimental emf from the calculated value was within the limits 1-2 mv.

Potentiometric titration was carried out in a cell with 3-5 membrane electrodes whose potentials were measured with respect to a calomel electrode. The solution being titrated was measured out by weight. The 5-6 electrodes tested for each resin, as a rule, gave coincident results.

Results of Potentiometric Titration of Acids. Electrodes in the hydrogen form, made from resins differing in chemical nature, were used for titrating acids (hydrochloric, sulfuric, and nitric).

Potentiometric titration curves of 1 N hydrochloric acid using different membrane electrodes are shown in Fig. 1. The amount in ml of alkali which corresponds to the equivalent point according to titration results obtained with an indicator is marked on the abscissa. Fig. 1 shows that the shape of the curve obtained depends on the type of ion exchange resin used for preparing the membranes. The curve obtained with membranes prepared from the hydroxyl resin R (Fig. 1, Curve 1) approximates the usual potentiometric titration curve obtained with a hydrogen electrode. An appreciable potential jump is observed at the end point in this case. There is a sharp change in potential naer the end point in the case of the membrance made form the carboxyl resin KB-4 (Curve 5), but there is still not a jump. The potential change near the end point is small in the case of electrodes made from the sulfo resins; the change can be established on the basis of the minimum on the curve.

Titration curves of 0.5 M sulfuric acid and 1 N nitric acid obtained on using electrodes made from the sulfo resins (SBS and KU-2) are shown in Fig. 2. The curves exhinit a clearly defined minimum at the end point, the minimum coinciding with the results of an indicator titration to an accuracy of 0.02 ml.

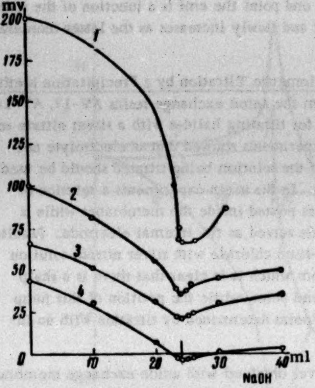

Fig. 3. Titration curves of 0.1 N hydrochloric acid (25 g) with 0.1046 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), SBS (curve 2), KU-2 (curve 3), and DKU-2 (curve 4).

During titration of 1 N solutions of acids, membranes in the hydrogen form were used with 0.1 N hydrochloric acid as an internal solution

Under these conditions, however, high results were obtained for 0.1 and 0.01 N hydrochloric acid when electrodes made from sulfo resins were used. The reason for the appearance of additional acidity in the solution may be the exchange of hydrogen ions from the membrane for sodium ions from the solution, which occurs during titration. In order to eliminate this effect, during titration of dilute solutions of acids electrodes made from sulfo resins were used in sodium form, while 0.1 M sodium chloride was used as the internal solution. When electrodes made from weakly acid resins are used during titration of dilute acid solution acidification of the solution following from exchange of hydrogen ions does not occur, and these membranes can be used in the hydrogen form.

Titration curves of 0.1 N hydrochloric acid using membrane electrodes made from sulfo resins in the sodium form are shown in Fig. 3. In this case the end points obtained from the potentiometric curves agree with the results obtained during titration with an indicator, while the character of the curve, as in the case of 1 N solutions, is determined by the type of resin from which the electrode is prepared.

Similar results were obtained for 0.01 N solutions of hydrochloric acid (Fig. 4). The accuracy of titration with membrane electrodes is a few tenths of a percent for all the concentrations studied.

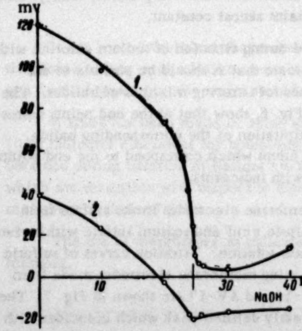

Fig. 4. Titration curves of 0.01 N hydrochloric acid (25 g) with 0.0101 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1) and SBS (curve 2).

Thus the experimental results show that membrane electrodes made from cation exchange resins in the hydrogen form can be successfully used for potentiometric titration of various acids (1-0.01 N) with aklali solutions. The character of the changes in emf during titration is determined by the acid strength of the active groups of the resin from which the membrane electrode is made. In the case of resins with weakly acid groups(the hydroxyl resin R and the carboxyl resin KB-4) there is a sufficiently sharp change in emf at the end point, corresponding to an appreciable change in pH at the titration end point (curve 1 in Figs. 1, 3, 4). The emf change from the beginning of a titration to the end point is 120-140 mv for electrodes prepared from resin R, the potential jump being 60-70 mv. For electrodes made from the carboxyl resin KB-4 the emf change up to the end point is about 90 mv (curve 5, Fig. 1). Such behavior on the part of electrodes made from weakly acid resins can be explained by the larger selectivity of these resins for hydrogen ions than for sodium ions The transition region from a hydrogen function to a sodium function, according to our results, lies within the PH range 4-7 for resin R and within the pH range 3-6 for the carboxyl resin.

The change in emf with addition of alkali in the case of electrodes made from the sufo resins can be explaind as follows. At the beginning of titration the membrane is in the hydrogen form , and its potential is determined by the hydrogen ion concentration. As alkali is added the membrane is gradually converted into the sodium form and reacts both to decreases in hydrogen ion concentration and to increases in sodium ion concentration. The nature of the curve obtained agrees with the ion exchange properties of sulfo resins,which do not exhibit selectivity toward hydrogen and other cations.

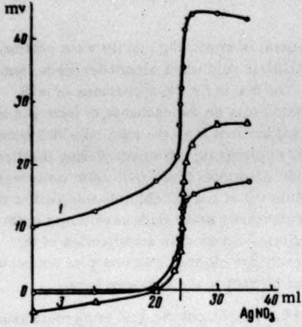

Fig. 5. Titration curves of 0.1 M sodium chloride (25 g) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins AV-16 (curve 1), and AV-17 (curve 2, 3).

The transition range from hydrogen function to a sodium function lies within the pH range 1.5-3.5 [7] for electrodes made from sulfo resins. After the end point the emf is a function of the sodium ion concentration only and slowly increases as the latter increases (excess alkali).

Results of Potentiometric Titration by a Precipitation Method. Membranes made from the anion exchange resins AV-17, AV-16, and EDE-10 were used for titrating halides with a silver nitrate solution. Preliminary experiments showed that an electrolyte not containing the anion of the solution being titrated should be used as the internal solution. In the main experiments a solution of 0.05 M sulfuric acid was poured inside the membranes while a micro calomel electrode served as the internal electrode. Results of titration of 0.1 M sodium chloride with silver nitrate solution are shown in Fig. 5, from which it is clear that there is a sharp potential jump at the end point, while the position of this jump coincides with the end point determined by titration with an indicator.

The titration curves obtained with anion exchange membranes are similar in character to the curve obtained with a silver chloride electrode. The value of the potential jump at the end point in the case where membrane electrodes are used, is however, less than that obtained when a silver chloride electrode is used. In this case the change in emf up to the end point is determined mainly by the concentration of chloride ions, and not by that of No_3— ions, since the exchange process proceeds at a comparatively slower rate on anion exchange membranes. The chloride ion concentration changes most sharply near the end point, and the result is a sharp change in potential. After the end point only NO_3^- ions are present in solution, but the transition to the new function proceeds slowly, and, accordingly, the emf remains almost constant.

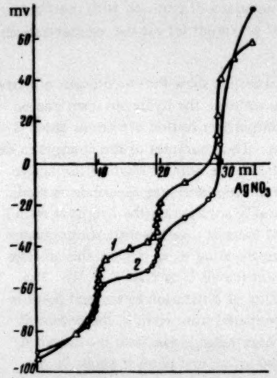

Fig. 6. Titration curves of chloride, bromide iodide (10 g of 0.1 M NaCl + 10 g 0.1 M NaBr + 10 g 0.1 M KI) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins EDE-10 (Curve 1) and AV-16 (curve 2).

The results obtained during titration of sodium chloride with silver nitrate solution indicate that it should be possible to use anion exchange membranes for titrating mixtures of halides. The titration curves shown in Fig. 6, show that at the end points corresponding to complete precipitation of the corresponding halide, there are clearly defined jumps which correspond to the end points obtained during titration with indicators.

Anion exchange membrane electrodes in the sulfate form were used for titrating sulfuric acid and sodium sulfate with barium chloride and barium acetate solution. Titration curves of sulfuric acid with barium acetate using membrane electrodes made from anion exchange resins AV-16 and AV-17 are shown in Fig. 7. The curves obtained have a clearly defined peak which coincides with an accuracy of a few tenths of a percent with the end point obtained during indicator titration. Up to the end point the emf is determined mainly by the SO_4^{2-} concentration,which changes most sharply at the titration end point; acetate ions hardly play any part because of the low dissociation of acetic acid. In order to compare the behavior of anion exchange membranes with cation exchange membranes during titration of sulfuric acid with a barium acetate solution, cation exchange membranes in the hydrogen form made from resin KU-2 (Fig. 7,curve 3) were used. At the end point the potential of the cation exchange membrane gives a sharp minimum, the presence of which is explained by the fact that during titration the hydrogen ion concentration decreases up to the end point as a result of the formation of the sparingly dissociated acid, and the emf decreases; after the end point the emf is deterimned by the barium ions, and the potential increases as the barium concentration increases.

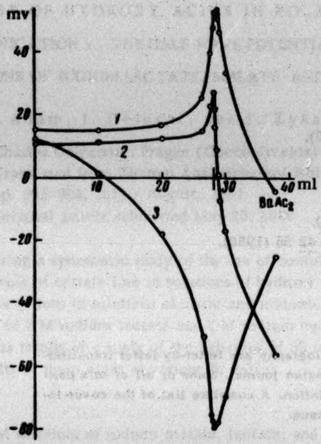

Fig. 7. Titration curves of 0.05 M sulfuric acid (50 g) with 0.1766 N barium acetate, using electrodes made from anion exchange resins EDE-10 (curve 1), AV-17 (curve 2), and cation exchange resin KU-2 (curve 3).

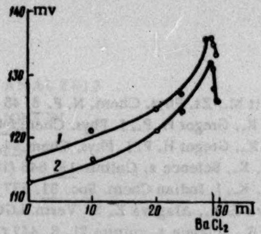

Fig. 8. Titration curves of 0.1 M sodium sulfate (25 g) with 0.1688 N barium chloride, using electrodes made from the anion exchange resin EDE-10 (curves 1, 2).

A most interesting case is titration of sodium sulfate with barium chloride solution (Fig. 8). Titration was carried out using anion exchange electrodes in the sulfate form; these electrodes react to changes in sulfate ion concentration, as a result of which there is a fairly sharp maximum peak at the end point.

SUMMARY

Membranes made from the sulfo cation exchange resins SBS, KU-2 and SDV-3, and from the carboxyl cation exchange resin KB-4 and the hydroxyl resin R, have been used as indicator electrodes for the potentiometric titration of acids. An explanation is given of the nature of the curves obtained during acid — alkali titration when membrane electrodes made from resins containing active groups differing in their chemical nature are used.

It has been established that membranes in the hydrogen form can be used for titrating concentrated acids. For titration of dilute acid solution, membranes made from the sodium form of strongly acidic resins and from the hydrogen form of weakly acidic resins should be used.

A study has been made of anion exchange membrane electrodes made from the resins AV-16, AV-17, and EDE-10 as indicator electrodes for potentiometric titration of halide and sulfate ions by precipitation methods. The curves obtained during titration of halides are similar in character to those obtained during titration with the usual electrodes which are reversible with respect to these ions. The titration curve obtained during titration of sulfate ions has a peak maximum at the end point.

The use of membranes as indicator electrodes opens up possibilities of potentiometric titration by precipitation methods.

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THE USE OF HYDROXY ACIDS IN POLAROGRAPHIC ANALYSIS

COMMUNICATION 1. THE HALF WAVE POTENTIALS OF CERTAIN IONS IN SOLUTIONS OF SODIUM LACTATE, MALATE AND SALICYLATE

I. Adam, J. Dolezal, and J. Zyka

Charles University, Prague (Czecholsvakia)

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During a systematic study of the use of complexing agents in polarographic analysis we became interested in the behavoir of certain ions in solutions of hydroxy acids. Breda et al [1] recently published the half wave potentials of a series of ions in solutions of citric and malonic acids, in solutions of the alkali salts of these acids, and also in mixtures of 1 M sodium lactate and 1 M sodium hydroxide. The work described here is a continuation of this research; it includes results of a study of the behavior of 35 ions in solutions of lactic, malic, and salicylic acids, and in solutions of the salts of these acids at various Ph values.

EXPERIMENTAL

1 M solutions of sodium malate, lactate, and salicylate were prepared from the pure acids; after adding a solution of the salt of the test element to the solution of the hydroxy acid, the pH was adjusted to the requisite value by addition of sodium hydroxide; the concentration of the test element in the final volume was 1×10^{-3}M. Solutions of the respective salts were prepared in most cases from analytical grade materials.

TABLE 1. Half Wave Potentials of Certain Ions in 1 M Soduim Lactate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	—0,44a	—0,45f	—0,58f	—0,67a
Cu^{2+}	—0,10b	—0,30b	—0,32b	—0,36a
As^{III}	h	h	0,0c	—0,14c
Sb^{III}	h	h	h	—0,12l
F_2^{3+}	h	—1,50b	—1,51b	—1,56b
CrO_4^{-2}	—0,91a	—0,88a	—0,84a	—0,84a
Mn^{2+}	h	f	f	f
Ni^{2+}	h	h	h	f
Co^{2+}	—1,47b	f	f	f
Zn^{2+}	—1,14b	—1,30; —1,46k	—1,34; —1,53k	—1,44b
UO_2^{2+}	e	e	e	e
Ti^{IV}	—1,35e	—1,41e	—1,53e	—1,60e
MoO_4^{2-}	i	i	h	h
VO_3	h	h	—1,19e	—1,25e
In^{3+}	—0,72b	h	h	h

Note. The following ions do not give a polarographic wave Ga^{III}, As^{V}, Sb^{V}, Sn^{II}, Sn^{IV}, Pd^{II}, Au^{III}, Pt^{IV}, Fe^{II} Ge^{IV}, WO_4^{2-}, Zr^{IV}, Ce^{III}, Ce^{IV}, Be^{II} Th^{IV}, Bi^{III}, Cd^{II}.

The polarographic curves were recorded on a Heyrovski Mark V 301 polarograph, using a 30 galvanometer and a Kalousek cell with a saturated calomel electrode.

The results obtained are presented in Tables 1-3. In addition to the value of the half wave potential, a short note on the polarographic behavior of individual ions is also included.

TABLE 2. Half Wave Potentials of Certain Ions in 1 M Sodium Malate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	−0,48a	−0,49a	−0,54a	−0,67a
Cu^{2+}	−0,10a	−0,14b	−0,20b	−0,22b
Sb^{V}	−0,84: −0,98k	−0,90d	−0,93d	−0,96a
Sn^{IV}	h	h	h	−1,19d
Fe^{3+}	−0,17g	−0,37g	−0,53g	−0,82g
CrO_4^{2-}	−0,30b	−0,27b	0,28b	−0,29b
Mn^{2+}	h	f	f	f
Zn^{2+}	−1,02;−1,22k	−1,36b	h	h
UO_2^{2+}	−0,42a	0,60d	0,63d	−0,67d
Ti^{IV}	−1,3d	−1,3f	−1,3f	−1,3f
MoO_4^{2+}	−1,28d	−1,30d	i	i
VO_3^-	−0,04b	−0,58b	h	h

Note. The following ions do not give a polarographic wave: Ni^{II}, Co^{II}, Ge^{IV}, In^{III}, Ga^{III}, As^{III}, As^{V}, Sn^{II}, Pd^{II}, Au^{III}, Pt^{IV}, WO_4^{2-}, Zn^{IV}, Ce^{III}, Ce^{IV}, Th^{IV}, Be^{II}, Bi^{III}, Cd^{II}.

TABLE 3. Half Wave Potentials of Certain Ions in 1 M Sodium Salicylate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	f	f	−0,60a	−0,63a
Cu^{2+}	f	i	i	e
As^{III}	h	h	h	−0,13c
Sb^{III}	h	h	h	−0,11l
Sb^{V}	f	f	−1,14b	−1,13a
Pd^{2+}	h	−0,6e	−0,62d	−0,66d
CrO_4^{2-}	−1,18b	−1,25d	−1,10d	−0,98b
Mn^{2+}	−1,53a	−1,58a	−1,64a	−1,75a
Ni^{2+}	−1,01d	−1,04d	−1,12d	−1,17d
Co^{2+}	−1,36a	−1,37b	−1,38; −1,55d	h
Zn^{2+}	−1,20d	−1,24d	−1,32d	−1,47d
UO_2^{2+}	−0,70; −1,15k	−0,72; −1,17k	−0,74; −1,20k	−0,81: −1,22k
Ti^{IV}	−0,87; −1,70k	−0,99; −1,39k	−1,15a	−1,32a
MoO_4^{2-}	i	h	h	h
VO_3^-	f	f	−1,32b	−1,68b
Ge^{IV}	−1,29b	−1,31b	−1,43b	−1,59b
In^{3+}	−0,58b	−0,73b	−0,89b	−1,12b

Note. The following ions do not give a polarographic wave: Fe^{II}, Fe^{III}, Ga^{III}, As^{V}, Sn^{II}, Sn^{IV}, Au^{III}, Pt^{IV}, WO_4^{2-}, Zr^{IV}, Ce^{IV}, Be^{II}, Th^{IV}, Ga^{III}, Bi^{III}, Cd^{II}.

Notes to Tables 1-3. a) well developed symmetrical wave with a diffusion character, suitable for analytical use; b) developed wave with a diffusion character; c) readily measured anodic wave suitable for analytical use; d) poorly developed double wave; only an approximate value for the half wave potential is given, this value being the mean of the half wave potentials of both waves; e) wave difficult to measure; f) precipitate formed; g) oxidation – reduction wave; h) the ion does not give a reduction wave in the given potential range; i) a drop in hydrogen overvoltage starts; k) a double wave is formed; l) anodic wave difficult to measure.

Half wave potentials were measured relative to a saturated calomel electrode.

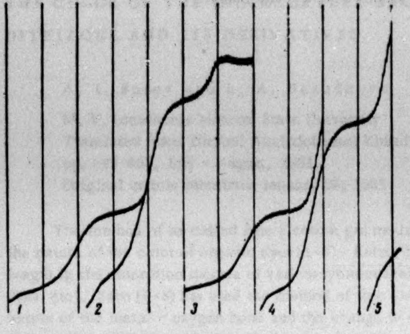

Fig. 1. Determination of nickel in cobalt. 1) 1 M sodium salicylate (9ml) + 0.01 M $NiSO_4$ (1 ml); 2) 1 M sodium salicylate (8ml) + 0.01 M $NiSO_4$ (1 ml) + 0.1 M $CaSO_4$ (1 ml); 3) 1 M sodium salicylate (8 ml) + 0.01 M $NiSO_4$ (1ml) + 1 M $CoSO_4$ (1 ml); 4) 1 M sodium salicylate (8 ml) + 0.01 M $NiSO_4$ (1 ml) + 1.55 g $CoSO_4$. Storage battery 2 v; S = 1/30; polarograms taken from − 0.8 v in a nitrogen atmosphere.

Possibilities of the Practical Use of Hydroxy Acids in Polarographic Analysis. It follows from the value of the half wave potentials found that it sould be possible to use hydroxy acids in polarographic practice. An interesting example is the possibility of determining nickel in the presence of cobalt. On the basis of preliminary results it should be possible to determine nickel even at a ratio of Ni : Co = 1 : 1000 in a supporting electrolyte of 1 M sodium salicylate (pH 12-14); under these conditions nickel gives a readily measured wave, while cobalt is not reduced. Since the nickel wave depends to some extent on the presence of cobalt in solution, the method of standards should be used. The experimental error in determining nickel does not exceed the usual experimental error of the polarographic method (Fig. 1).

Another interesting example is the possibility of determining iron in the presence of high concentrations of manganese by using a supporting electrolyte of 1 M sodium malate (pH 8-9). Despite the fact that at high manganese concentrations in the given medium a precipitate is formed, the iron is not adsorbed. Fig. 2 shows some polarograms of a solution containing iron and manganese, the latter at a comparatively high concentration; the method of standard additions is used. Cu^{2+}, CrO_4^{2}, Pb^{2+}, and UO_2^{2+} ions interfere with iron determination.

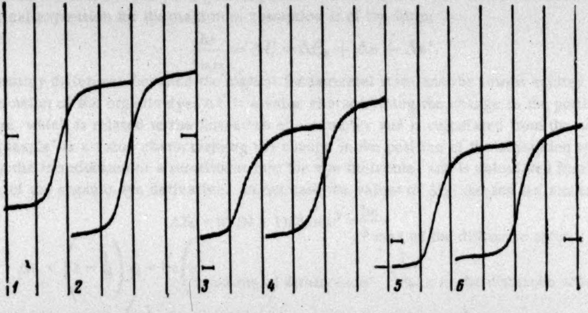

Fig. 2. Polarograms demonstrating the possibility of determining iron in the presence of manganese. Supporting electrolyte 1 M sodium malate (pH 9) (8 ml) + 1 M $MnSO_4$ (1 ml). 1) Electrolyte + 1.094 mg Fe^{2+}; 2) electrolyte + 0.250 mg Fe^{2+}; 3) electrolyte + 0.469 mg Fe^{3+}; 4) electrolyte + 0.091 mg Fe^{3+}; 5) electrolyte + 1.016 mg Fe^{2+} + Fe^{3+}; 6) electrolyte + 0.047 Fe^{3+}. Storage battery 2 v; S = 1/30; polarograms taken from − 0.1 v (saturated calomel electrode) in a nitrogen atmosphere.

SUMMARY

A study has been made of the behavior of 35 ions in solutions of latic, malic, and salicylic acids, and in solutions of the salts of these acids, and their half wave potentials have been determined. The results obtained show that it should be possible to determine iron analytically in the presence of large amounts of manganese in an alkaline solution of sodium malate.

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THE COLOR OF THE INNERCOMPLEX SALTS OF BISMUTH WITH DITHIZONE AND ITS DERIVATIVES

A. I. Busev and L. A. Bazhanova

M. V. Lomonosov Moscow State University

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The method of so-called free electron gas models has proved to be the most successful approach for explaining the nature of the color of organic dyes [1-5]. Kuhn [2] has adopted this method for calculating the maximum wave length in the absorption spectra of various symmetrical and unsymmetrical organic dyes (triphenylmethane, anthracene dyes, etc). Sano [6-8] has used the method of free electron gas models for explaining the relationship between the nature of the metal − oxygen bond and the change in color of a reagent during complex formation. The author calculated the maximum wavelengths in the absorption spectra of complexes of phenylfluorone derivatives with Group IV elements, and also quantitatively evaluated the value of the polarity of the metal − oxygen bond for the phenylfluoronates of the same elements. As the ionic character of this bond increases, the absorption maximum of the metal phenylfluoronate shifts toward the longer wavelengths, i.e. toward the absorption maximum of the reagent anion.

We have applied the method indicated to the innercomplex compounds of bismuth with 1, 5-diphenylthiocarbazone (dithizone) derivatives. We calculated the maximum wavelengths of the absorption of solutions of the complexes formed between bismuth and dithizone derivatives in a number of organic solvents. The calculated values were found to be in good agreement with the experimentally determined wavelengths of the absorption maxima of the same complexes of bismuth with dithizone derivatives can be calculated when the maximum absorption wavelengths of the dithizone anion and of the anion of the corresponding dithizone derivative and bismuth dithizonate are known. The general mathematical expression for the maximum absorption is of the form:

$$\frac{hc}{\lambda_{\max}} = \Delta E = \Delta E_0 + \Delta\varepsilon + \Delta\varepsilon', \qquad (1)$$

where ΔE_0 is the energy difference between the highest fundamental state and the lowest excited state of the free electron gas in the anion of the organic dye; $\Delta\epsilon$ is a value characterizing the change in the position of the absorption spectrum of the dye which is related to the formation of a complex and is calculated from the absorption maximum of the metal complex; $\Delta\epsilon'$ is a value characterizing the change in the position of the absorption spectrum of the dye which is caused by the introduction of a substituent into the dye molecule, and is calculated from the absorption maximum of the anion of the organic dye derivative. In our case the values of ΔE_0, $\Delta\epsilon$ and $\Delta\epsilon'$ are expressed as follows:

$$\Delta E_0 = h^2 (N+1)/8mcL^2 = \frac{hc}{\lambda_{\max\text{ of the dithizone anion}}}$$

$$\Delta\epsilon = \left(1 - \frac{1}{N}\right) v_0 = hc\left(\frac{1}{\lambda_{\max\text{ metal dithizonate}}} - \frac{1}{\lambda_{\max\text{ of the dithizone anion}}}\right)^{*}$$

$$\Delta\epsilon' = 4v_1 a{;}L = hc\left(\frac{1}{\lambda_{\max\text{ anion of the dithizone derivative}}} - \frac{1}{\lambda_{\max\text{ of the dithizone anion}}}\right)^{*},$$

where N is the number of π-electrons in the chain of the dithizone molecule ($N = 2j + 2$, where j is the number of double bonds in the chain of the dithizone molecule), m is the mass of an electron, c is the velocity of light, h is Planck's constant, L is the length of the chain of the organic dye, v_0 is the potential energy of the movement of π-electrons along the chain L; v_1 and a characterize the change in potential energy of the π-electrons on introducing a substituent into the molecule of the organic dye**. From equation (1), by substituting the value of each member, we obtain the following simple relation for calculating the absorption maximum of solutions of the complexes of bismuth with dithizone derivatives:

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* The formula given in [7] is incorrect.

** For the physical significance of v_1, a, v_0, etc see [2, 4].

$$\frac{1}{\lambda_{\max}} = \frac{1}{\lambda_{\max} \text{ of bismuth dithizonate}} + \frac{1}{\lambda_{\max} \text{ of the anion of the dithizone derivative}} - \frac{1}{\lambda_{\max} \text{ of the dithizone anion}} \qquad (2)$$

Our problem consisted, therefore, in finding the absorption maxima of the anionic forms of dithizone, of its derivatives, and of bismuth dithizonate, and calculating by means of formula (2) the absorption maxima of solutions of the complexes of bismuth with dithizone derivatives in an organic solvent.

EXPERIMENTAL

Reagents. 1. The stock solution of bismuth nitrate was prepared by dissolving analytical grade $Bi(NO_3)_3 \cdot 5H_2O$ in dilute nitric acid. The concentration of the solution was established by three gravimetric methods: phosphate, 8-hydroxyquinoline, and ammoniacal methods [9]. One ml of the solution prepared was found to contain 20.82 mg Bi. Working solutions were prepared by suitable dilution of the stock solution.

2. Dithizone was purified by Markova's method [10].

3. The dithizone derivatives were prepared by formazyl method [11-13].

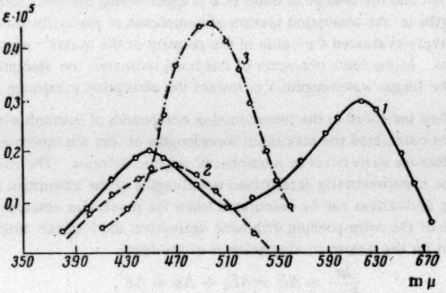

Fig. 1. Absorption spectra of the anionic (Dz^-) and molecular (HDz) forms of dithizone and of its complex with bismuth ($BiDz_3$). 1) HDz in CCl_4; 2) Dz^- in 0.7 M NaOH; 3) $BiDz_3$ in CCl_4.

The solutions of the thiocarbazones in organic solvents had a concentration of $1 \cdot 10^{-4}$ M.

4. The organic solvents were purified by distillation and their purity checked by refractive index n_D^{20} measurements.

5. NaOH, 0.7 N solution.

The optical density of the solutions was measured on a SF-4 spectrophotometer using cylindrical cells with l = 4.11 mm, relative to the pure solvent.

We obtained the absorption spectra of solutions of the thiocarbazones and of their complexes with bismuth in organic solvents, and also the absorption spectra of the anionic forms of the thiocarbozones in 0.7 N sodium hydroxide. Extraction of bismuth with the thiocarbazones was carried out at the optimum pH value of 6-8 which we had established earlier.

In Figs. 1 and 2 are shown the absorption spectra of solutions of dithizone and of p-tolylthiocarbazone in their ionic (in 0.7 N NaOH) and molecular (in CCl_4 solution) forms, as well as the absorption spectra of solutions of their complexes with bismuth. The absorption spectrum of the complex is intermediate between the absorption spectra of the corresponding thiocarbazone in its ionic and molecular forms (here and for the rest of the article, when we refer to the molecular form of thiocarbazone we shall only have the ketonic form in mind).

The difference in the absorption maxima of the thiocarbazones in their acid and alkali forms lies within the range 150-160 mμ (Table 1).

TABLE 1. Absorption Maxima of Thiocarbazones in their Acid (Ketone) and Alkali Forms (mμ)

Reagent	Acid form, λ_1,mμ	Alkali form, λ_2,mμ	$\lambda_1-\lambda_2$, mμ
1,5-Diphenylthiocarbazone	620	470	150
p-Tolylthiocarbazone	632	480	152
o-Tolylthiocarbazone	630	470	160
β-Naphthylthiocarbazone	660	500	160
α-Naphthylthiocarbazone	665	500	165
p-Chlorothiocarbazone	635	480	155
p-Bromothiocarbazone	638	480	158
p-Iodothiocarbazone	645	490	155
o-Iodothiocarbazone	640	475	165
p-Anisylthiocarbazone	640	485	155
o-Anisylthiocarbazone	645	490	155
p-Nitrothiocarbzone	*	505	–

* p-Nitrothiocarbazone is represented in solution only as the enol form with a maximum absorption at 455 mμ.

Table 2 contains the absorption maxima of the complexes of bismuth with dithizone derivatives calculated by means of formula (2) and found experimentally for solutions in carbon tetrachloride, benzene, and chloroform; the absorption maximum of the complex of bismuth with p-nitrothiocarbazone is given for its solutions in nitrobenzene.

In the case of the thiocarbazones studied therefore, we observe a phenomenon which is contrary to that observed in the case of other known organic reagents: the anionic form of most known organic dye-reagents has a deeper color than the acid form. Since, during complex formation, a radical – metal bond develops which is more polar than the radical – reagent -H bond (i.e. the ionic character of the bond increases), the complex has a deeper color than the acid form, and a less intense color than the alkali form of the reagent. In the case of the thiocarbazones on the other hand the anionic form has a less intense color than the acid (ketonic) form, and complex formation leads to a shift in the absorption maximum of the acid form of the reagent toward the short wave side of the spectrum.

It is clear from Tables 1 and 2 that the shift in the absorption maxima of the complexes of bismuth with thiocarbazone with respect to the anionic form of the reagent is a constant, in all cases equal to 20-25 mμ. The innercomplex salts of bismuth with dithizone and its derivatives are more intensely colored than the color of the corresponding reagent in the anionic form, thus: a yellow colored anion corresponds to an orange colored complex (dithizone, o-tolylthiocarbazone), an orange colored anion corresponds toa red-rose colored complex (p-tolyl, p-, o-anisyl-, p-iodothiocarbazones), while a rose colored anion corresponds to a raspberry colored complex (α- and β-naphthylthiocarbazones).

In order to compare the color of solutions of the innercomplex salts of bismuth with the thiocarbazones with that of the corresponding solid salts, we prepared the salts of bismuth with dithizone, β-naphthyl-, p-tolyl-, and

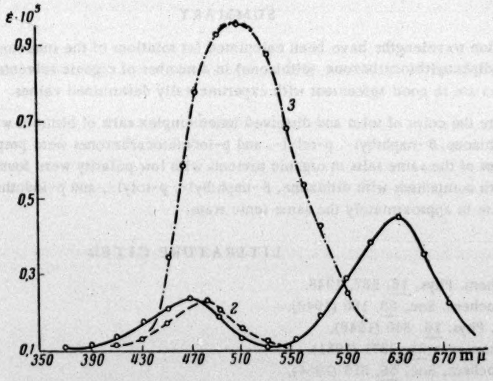

Fig. 2. Absorption spectra of the anionic (R^-) and molecular (HR) forms of p-tolylthiocarbazone and of its complex with bismuth (BiR_3) 1) HR in CCl_4; 2) R^- in 0.7 M NaOH; 3) BiR_3 in CCl_4.

TABLE 2. Absorption Maxima of Solutions of the Complexes of Bismuth with Derivatives of 1,5-Diphenylthiocarbazone (Dithizone) (A) (the Experimentally Determined Absorption Maximum of Bismuth Dithizonate in CCl_4, $CHCl_3$, and C_6H_6 was Found at 4950 A, while in Nitrobenzene it was found at 5000 A)

Reagent / Solvent	CCl_4		C_6H_6		$CHCl_3$		Nitrobenzene	
	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated
p-Tolylthiocarbazone	5050	5055	5050	5055	5050	5055	–	–
o-Tolylthiocarbazone	4900	4950	–	–	–	–	–	–
β-Naphthylthiocarbazone	5200	5266	5250	5266	5250	5266	–	–
α-Naphthylthiocarbazone	5200	5266	–	–	–	–	–	–
p-Chlorothiocarbazone	5050	5055	5050	5055	5050	5055	–	–
p-Bromothiocarbazone	5000	5055	–	–	–	–	–	–
p-Iodothiocarbazone	5050	5160	5100	5160	5100	5160	–	–
o-Iodothiocarbazone	4950	5002	–	–	–	–	–	–
p-Anisylthiocarbazone	5100	5107	5100	5107	5100	5107	–	–
o-Anisylthiocarbazone	5105	5160	–	–	5150	5160	–	–
p-Nitrothiocarbazone	–	–	–	–	–	–	5350	5373

p-iodothiocarbazones in the solid form according to the following methods [14].

Excess $Bi(ClO_4)_3$ was added to an acetone solution of the thiocarbazone and the mixture allowed to stand until complete deposition of precipitate had occured. The precipitate was filtered off, washed with water, and dried in a desiccator over sulfuric acid. The innercomplex salts formed between bismuth and the thiocarbazones had a metallic lustre, their color in the solid from corresponding to that in organic solvents (because of the high color intensity, in order to establish the color of the bismuth salts with the thiocarbazone, they were ground with NaCl).

The absorption maximum of a solution of the solid salt of bismuth with a thiocarbazone coincides with that of the corresponding salt obtained by direct extraction of bismuth with a solution of the thiocarbazone in an organic solvent. Comparison of the results obtained allows one to suggest that the nature of the bond between bismuth and the radical in the compounds with dithizone and its derivatives is approximately the same, both in the form of solutions in solvents of low polarity, and in the solid state.

SUMMARY

Maximum absorption wavelengths have been calculated for solutions of the innercomplex salts of bismuth with derivatives of 1, 5-diphenylthiocarbazone (dithizone) in a number of organic solvents. The calculated values of the absorption maxima are in good agreement with experimentally determined values.

In order to compare the color of solid and dissolved innercomplex salts of bismuth with thiocarbazones, solid salts of bismuth with dithizone, β-naphthyl-, p-tolyl-, and p-iodothiocarbazones were prepared. The color of the solid salts and of solutions of the same salts in organic sovlents with low polarity were found to be almost identical in the case of the bismuth compounds with dithizone, β-naphthyl-, p-tolyl-, and p-iodothiocarbazones; i.e. the solid and dissolved salt are in approximately the same ionic state.

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A NEW COMPLEXOMETRIC METHOD FOR DETERMINING SULFATES IN THE PRESENCE OF CALCIUM AND MAGNESIUM

Ioan Dragusin*
Ploesti (Rumania)

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Previously we have described several methods for the complexometric determination of barium and sulfates using sodium rhodizonate as indicator [1]. During determination of sulfates in solutions containing calcium and magnesium, the sulfates were removed as $BaSO_4$, the latter was dissolved in excess of the latter back-titrated with barium chloride solution.

In order to develop a simpler and more rapid method which would not require separation of sulfates as $BaSO_4$, we adopted Casini's method [2] as a basis, and modified it by replacing the complexometric titration based on neutralization with acid-base indicators, with complexometric titration in the presence of indicators which are specific for the ions it is required to determine in solution. The method developed permits determination of total Ca + Mg on an aliquot of test solution, titration being carried out with EDTA-Na in the presence of eriochrome black T; on another aliquot of solution, after precipitation of sulfates with a known amount of barium chloride, the total content of calcium, magnesium, and barium remaining in solution is titrated with a solution of EDTA-Na in the presence of sodium rhodizonate. In this way total $Ca + Mg + Ba - SO_4$ is determined. Knowing the total content of Ca + Mg, the sulfate content of the solution can be calculated.

Although the method modified in this way permits the sulfate content to be determined readily with reasonable accuracy, there is still the drawback that one had to work with another indicator and with another solution of complexon in each of the two titrations.

It has been shown earlier [1], that after dissolving the barium sulfate in excess EDTA-Na ($Na_4T + BaSO_4 \rightarrow Na_2BaT + Na_2SO_4$), on titrating excess of the complexon with barium chloride solution, also added in an amount which is in excess of that required for reaching the equivalence point, the barium sulfate is not precipitated again. Under these condtitions the solution remains completely clear. When a solution containing barium sulfate dissolved in excess complexon is used for titrating any solution of barium chloride, formation of $BaSO_4$ is not observed, probably as the result of the formation of a compound containing Ba^{2+}, SO_4^{2-} ions and ethylenediaminetetracetic acid.

The method developed for the determination of sulfates in the presence of calcium and magnesium is based on the use of this phenomenon; the method is distinguished by its rapidity and simplicity. Taking into account that the stability of the complexonates of the alkaline earth metals decreases in the series Ca > Mg > Ba, their sum can be determined by complexometric titration in the presence of an indicator for Ba^{2+} ions, sodium rhodizonate. The results obtained are accurate and reproducible (Table 1).

Table 1. Determination of $Ca^{2+} + Mg^{2+} + Ba^{2+}$ in the Presence of Sodium Rhodizonate

Content (equivalents)				Totally determined components (equivalents)
Ca^{2+}	Mg^{2+}	Ba^{2+}	Total	
0,0015	—	0,0050	0,0065	0,00650
0,0020	—	0,0050	0,0070	0,00698
0,0025	—	0,0050	0,0075	0,00750
—	0,0010	0,0050	0,0060	0,00599
—	0,0015	0,0050	0,0065	0,00650
—	0,0025	0,0050	0,0075	0,00750
0,0025	0,0010	0,0050	0,0085	0,00862
0,0040	0,0020	0,0050	0,0110	0,01101
0,0040	0,0020	0,0100	0,0160	0,01605
0,0050	0,0030	0,0100	0,0180	0,0182

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* Translated from French by P. K. Agasyan.

When a known amount of barium chloride solution taken in excess is added to solutions containing calcium and magnesium in the presence of sulfates, $BaSO_4$ is precipitated in an amount corresponding to the sulfate content; further complexometric titration gives the value of total Ca + Mg + Ba − SO_4 (1).

But if a known amount of complexon solution greater than that which corresponds to the sulfate content is added to the test solution, the sulfate ions will be masked, so that on addition of excess barium chloride solution the test solution remains completely clear, as if there were no sulfate ions present at all in solution.

By continuing titration with complexon solution the value of total Ca + Mg + Mg (II) is obtained. Since the amount of barium chloride added is known, it is possible to find total Ca + Mg by difference.

The sulfate content is determined by the difference between the values II and I.

Reagents Used. 0.05N Tetrasodium ethylenediaminetetracetate solution. 9.3063 g EDTA-Na and 1.9-1.95 g of granulated NaOH are dissolved in a small amount of distilled water in a one liter standard flask, and the volume made up to the mark with distilled water. It is standardized against standard barium chloride solution.

Indicator Solution. About 20-30 mg of sodium rhodizonate is shaken up with 2 ml of distilled water. The solution should be prepared daily.

1% Alkali Blue Solution. An approximately 1% aqueous solution of alkali blue is prepared.

Buffer Solution. This consists of 200 ml of a solution containing 2 g ammonium chloride and 25 ml of a 25% ammonia solution.

Analytical Procedure. In order to check the method, two aliquots of a neutral or a weakly acid solution containing known amounts of sulfate, calcium, and magnesium are taken and diluted to a volume of about 100 ml.

A known excess of 0.05 N barium chloride (20-25 ml) is added to the first aliquot, the liquid is boiled for 2-3 min until the sulfate has been completely precipitated as $BaSO_4$, and then cooled to room temperature. A few drops of sodium rhodizonate solution is added until the characteristic rose color appears, 3 ml of buffer solution is then added, followed by alkali blue solution until the test solution has a bluish-violet color. The solution is titrated with 0.05 N EDTA-Na solution to the equivalence point, where the color of the solution changes to a pure green as a result of the superposition of the supplementary colors of the indicators [1].

The amount of EDTA-Na used up in this titration (A ml) corresponds to the content of Ca + Mg + Ba − SO_4.

To the second aliquot is added an accurately measured volume of EDTA-Na, the amount added being less than that used for titrating the first aliquot. Buffer solution is then added, followed by the same amount of barium chloride as that added to the first aliquot, and the sodium rhodizonate and alkali blue solutions. Since precipitation of sulfate is prevented in this case, titration of the completely clear solution with the standard EDTA-Na solution measured out from the same buret is continued until the color of the test solution changes to a pure green color. The total of EDTA-Na solution used in this case (B ml) is greater than the volume used in titrating the first aliquot, and corresponds to its content of Ca + Mg + Ba.

The sulfate content is calculated by means of the following equation:

$$SO_4^{2-} = (B - A) \cdot 0.0024016 \text{ g in the test material.}$$

Since the amount of 0.05 N bairum chloride added to the aliquots is known, total Ca + Mg is found by difference, using the results obtained during titration of the second aliquot. The calcium, magnesium and sulfate content can be determined from the results of a complexometric titration of calcium in a new, separate aliquot of the test solution in the presence of murexide.

Table 2 contains results for the determination of sulfate in dilute solutions containing various amounts of calcium and magnesium.

Application of the Method for the Analysis of Natural Water. The method suggested has been successfully used for the determination of sulfate in drinking and industrial water, which usually, in addition to the alkali and alkaline earth metals, also contain some iron and traces of other materials which do not appreciably affect the experimental results.

The bicarbonate content, i.e. the temporary hardness, is determined first by titrating 100 ml of water with 0.1 N hydrochloric acid in the presence of methyl orange. Hydrochloric acid in an amount 0.1-0.2 ml greater than that

TABLE 2. Determination of sulfate in the Presence of Calcium and Magnesium

SO_4^{2-} content of the test sample, g	
Taken	Found complexometrically
0,00240	0,00245
0,00480	0,00492
0,00960	0,00970
0,01200	0,01200
0,04803	0,04827

TABLE 3. Determination of the Sulfate Content of Natural Water

SO_4^{2-} found, g/liter	
Gravimetrically	Complexometrically
0,03404	0,03362
0,05041	0,05043
0,05620	0,05380
0,04632	0,04528
0,05280	0,05043

used in the bicarbonate determination is added to another sample and the liquid heated for 2-3 min. After cooling to room temperature the sulfate, calcium, and magnesium content is determined as described above.

In this way the sulfate, bicarbontae, calcium, and magnesium contents are determined,as well as the hardness of the water (temporary, permanent, and total).

Results of the determination of sulfate in drinking and industrial water by the suggested method and by the classical gravimetric method are compared in Table 3.

SUMMARY

A new, rapid, and accurate method has been developed for the determination of sulfate in the presence of calcium and magnesium.

The method has been successfully used for the analysis of drinking and industrial water, and good results have been obtained; in addition, this method has the advantage that it is possible to determine total Ca + Mg by the same procedure.

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DETERMINATION OF MICROAMOUNTS OF COPPER IN WATER, SOILS, AND BIOLOGICAL MATERIALS BY MEANS OF NICKEL DIETHYLDITHIOPHOSPHATE

A. A. Nemodruk and V. V. Stasyuchenko

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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A large number of methods have been suggested for the determination of copper in water, soils, and materials of plant and animal origin [1-12]. Of these methods the most widely used are photometric methods [1-4, 6-8, 10, 12], and in particular the method involving sodium diethyldithiocarbamate [4, 7, 10]. This latter reagent, however, is not specific enough and is inferior in this respect to a number of other reagents, including diphenylcarbazone [1], potassium or nickel diethyldithiophosphate [2, 13], and 2,2'-diquinolyl [3]. Comparative determination of copper by means of the three reagents indicated, in soils and plants, has shown that good results can be obtained only when the first two reagents are used. In order to determine copper by means of 2,2'-diquinolyl it is necessary to remove most of the interfering elements beforehand. In this connection therefore we have only examined in detail the two methods involving diphenylcarbazone [1] and nickel diethyldithiophosphate with respect to their application to the determination of small amounts of copper in water, soils, and biological materials.

In the course of the work described here, it was established that the presence of nitric acid in the solutions obtained after decomposition of samples of soil or plant material interferes with the determination of copper by means of nickel diethyldithiophosphate. The results obtained in the presence of nitric acid are low. Thus during determination of copper in plant material in which 10 ml of dilute nitric acid (1:2) was used for treating the ash obtained after combustion and calcining of an aliquot, the results were found to be 10-15% lower than those obtained for the same material during other experiments in which the nitric acid was removed beforehand from the solution (by adding concentrated sulfuric acid and evaporating to the appearance of white fumes of H_2SO_4). Nitric acid interferes in the same way during determination of copper in soils.

The optimum concentration of reagent added was establihsed by making the folllowing slight modification to the method of determining copper in soils and biological materials by means of nickel diethyldithiophosphate [2]. Busev and Ivanyutin [2, 13] have shown that one essential drawback in the determination of copper by means of potassium or nickel diethyldithiophosphate is the partial conversion under certain conditions of cupric diethyldithiophosphate into cuprous diethyldithiophosphate, this being accompanied by a drop in the intensity of the yellow color of the solution. They also established that this conversion only proceeds at an appreciable rate in the presence of appreciable concentrations of copper and pottasium or nickel diethyldithiophosphate, and that when working with soolutions whose copper concentration does not exceed 2 mg/liter and whose nickel diethyldithiophosphate concentration is not greater than 0.001 M, this conversion does not effect the results for copper. It was established, however, that for determination of 5-40 μg of copper, addition of 1.5-2.0 ml of 0.005 M nickel diethyldithiophosphate ensured the most reproducible and accurate results. Table 1 contains results for the determination of copper in two soil samples in which various amounts of reagent were used; they show that the amount of nickel diethyldithiophosphate indicated above is the optimum amount.

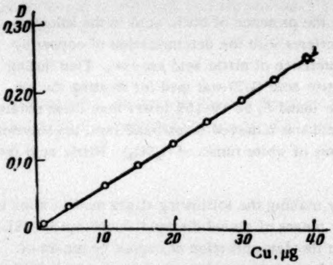
In addition to establishing the amount of reagent to be added more accurately, some other modifications were made to Busev and Ivanyutin's method [2] which enabled the time of a determination to be shortened. Copper was finally determined in soils, water, and biological materials by the following method.

For determination of copper in soils, 1-2 g of finely ground (the particle size should not exceed 0.1 mm) air-dry material is calcined in a procelain crucible at a dark-red heat (550°) for 2 hr. After cooling, 20-30 ml of a mixture

Table 1. Accuracy and Reproducibility of the Results of Copper Determination in Soils by Busev and Ivanyutin's method [2] as a Function of the Amount of Reagent Added*

Soil Sample No. 1				Soil Sample No. 2			
Cu added, µg	Amt. of 0,005 M nickel diethyldithiophosphate s. sol. added ml	Cu found µg	Error %	Cu added µg	Amt. of 0,005 M nickel diethyldithiophosphate sol. added ml	Cu found µg	Error %
—	15	20,7	—	—	15	13,8	—
5	15	24,1	—6,1	5	15	17,9	—4,8
10	15	27,6	—10,1	10	15	21,6	—9,2
—	10	21,3	—	—	10	14,1	—
5	10	24,9	—5,3	5	10	18,0	—5,8
10	10	29,0	—7,3	10	10	22,1	—8,7
—	5	21,5	—	—	5	14,4	—
5	5	25,8	—2,6	5	5	18,8	—3,1
10	5	29,8	—5,6	10	5	22,9	—6,1
—	3	21,6	—	—	3	14,6	—
5	3	26,9	+1,1	5	3	19,3	—1,5
10	3	30,7	—2,8	10	3	24,3	—1,2
—	2	21,5	—	—	2	14,6	—
5	2	26,7	—0,8	5	2	19,4	—1,0
10	2	31,2	—1,0	10	2	25.0	+1,6
—	1,5	21,6	—	—	1,5	14,5	—
5	1,5	26,9	+1,1	5	1,5	19,9	+2,0
10	1,5	31,8	+0,7	10	1,5	24,1	—1,6

* In each series of three determinations the weight of soil taken was 2 g; the volume of solution after decomposition was made up to 200 ml, and 50 ml of this solution was used for each determination.



Calibration curve for photometric determination of copper.

of concentrated hydrochloric and nitric acids (3:1) is added, and the mixture is heated on a sand bath until almost all the liquid phase has been removed by evaporation. Two ml of concentrated sulfuric acid is added to the residue and heating continued until white fumes of H_2SO_4 start to come off. After cooling, 40-60 ml of water is added and the whole boiled for 10-15 min to dissolve the salts which separate out; the solution is then filtered free from the insoluble residue*. The filter is washed with hot water weakly acidified with sulfuric acid (2 ml of concentrated H_2SO_4 per 500 ml water), the wash liquors are combined with the filtrate and the copper content determined as described below.

For determination of copper in materials of plant or animal origin, a sample containing 5-100 µg copper is dried and calcined at a dark-red heat (550°). The ash is dissolved in aqua regia, the liquid is evaporated on a sand bath until almost all the liquid phase has been removed, and the procedure outlined for soil analysis then followed. The sulfuric acid filtrate which has been transferred to a 100 or 200 ml standard flask is diluted with water to the mark; 50 ml of this solution is transferred to a separating funnel**, 10 ml of CCl_4 is added, followed by 1.5-2.0 ml of 0.005 M aqueous nickel diethylidithiophosphate which is added slowly, dropwise and with stirring. The copper diethyldithiophosphate which is formed is extracted by vigorous shaking of the funnel for one minute. After the phases have separated, the organic phase is filtered through a dry filter into a cell with a path length of 1 or 2 cm, and the optical density measured on a FEK-M electrophotocolorimeter fitted with a blue filter, a blank being used as reference solution. The copper content is found by means of a calibrtaion curve (see diagram).

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* In order to filter off the insoluble material and silica more rapidly it is advisable to filter through a paper mass supported on a perforated glass plate, in a funnel, the lower part of which is filled with water.

** When the test sample contains less than 25 µ g Cu, all the filtrate, without preliminary dilution in a standard flask, is transferred to the separating funnel.

Table 2. Results of the Determination of Copper in Soils, Plant Materials, and water

Test material	Copper added μg	Total amount of copper μg	Copper found μg	Error %
Black earth from Kursk, upper layer (0-10 cm) (sample wt. 1 g)	—	—	27,7	—
	5,0	32,7	32,0	—2,1
	10,0	37,7	39,0	+3,4
	15,0	42,7	41,6	—2,6
Ditto, layer taken at a depth of 30-40 cm (sample wt. 1 g)	—	—	26,6	—
	5,0	31,6	32,0	+1,3
	10,0	36,6	35,1	—4,1
	15,0	41,6	43,0	+3.4
Ditto, layer taken at a depth of 172-182 cm (sample wt. 1 g)	—	—	21,0	—
	5,0	26,0	25,0	—3,8
	10,0	31,0	30,3	—2,3
	15,0	36,0	37,5	+4,2
Clover (sample wt. 7.4 g)	—	—	28,6	—
	5,0	33,6	34,2	+1,8
	10,0	38,6	39,0	+1,0
	15,0	43,6	42,6	—2,3
Tap water, Moscow, Rublevskii Reservior (sample volume one liter)	—	—	14,7	—
	10,0	24,7	24,6	—0,4
	20,0	34,7	33,3	—4,0

TABLE 3. Results of Copper in Soils

Soil sample	Copper content. found		Deviation %
	By Lapin and Makarova's method [1], %	By means of nickel diethyl-dithiophosphate, %	
PK -1	$4,00 \cdot 10^{-3}$ $3,80 \cdot 10^{-3}$	$4,04 \cdot 10^{-3}$ $3,92 \cdot 10^{-3}$	
	Mean $3,90 \cdot 10^{-3}$	$3,98 \cdot 10^{-3}$	2,1
PK -2	$3,30 \cdot 10^{-3}$ $3,02 \cdot 10^{-3}$	$3,36 \cdot 10^{-3}$ $3,30 \cdot 10^{-3}$	
	Mean $3,16 \cdot 10^{-3}$	$3,33 \cdot 10^{-3}$	5,4
PK -3	$3,80 \cdot 10^{-3}$ $3,97 \cdot 10^{-3}$	$4,10 \cdot 10^{-3}$ $4,06 \cdot 10^{-3}$	
	Mean $3,89 \cdot 10^{-3}$	$4,08 \cdot 10^{-3}$	5,0
PK -4	$3,60 \cdot 10^{-3}$ $3,85 \cdot 10^{-3}$	$3,84 \cdot 10^{-3}$ $3,95 \cdot 10^{-3}$	
	Mean $3,73 \cdot 10^{-3}$	$3,89 \cdot 10^{-3}$	4,3
PK-5	$3,35 \cdot 10^{-3}$ $3,23 \cdot 10^{-3}$	$3,48 \cdot 10^{-3}$ $3,35 \cdot 10^{-3}$	
	Mean $3,29 \cdot 10^{-3}$	$3,41 \cdot 10^{-3}$	3,6
PK-6	$2,83 \cdot 10^{-3}$ $3,02 \cdot 10^{-3}$	$3,01 \cdot 10^{-3}$ $3,11 \cdot 10^{-3}$	
	Mean $2,93 \cdot 10^{-3}$	$3,06 \cdot 10^{-3}$	4,4

For determination of copper in water, one liter of test water is acidified with 20 ml of 6 N H_2SO_4 and then heated at 80-100°* for 30 min. After cooling, 10 ml of CCl_4, and 2 ml of 0.005 M nickel diethyldithiophosphate are added and the whole shaken for 5 min. After standing for a short time (to enable the phases to separate) the organic layer is filtered through a dry paper filter into a cell, and its optical density measured. The copper content is determined by means of a calibration curve.

A calibration curve is constructed as follows: 0.3928 g of cupic sulfate (chemically pure grade) is dissolved in water to which 10 ml of 6 N sulfuric acid has been added, and the volume made up to the mark with water in a 1000 ml standard flask; 100 ml of this solution is transferred to another 1000 ml standard flask and the volume again made up to the mark with water. The copper content of this final solution is 10 μg/ml. Fifty ml of water and 2 ml of 6 N H_2SO_4 are added to each of 10 separating funnels; into these funnels, apart from the first, is then introduced 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 respectively of the standard copper solution (10 μg Cu/ml); finally 10 ml of CCl_4 is added to each funnel. 2.0 ml of 0.005 M nickel diethyldithiophosphate is added dropwise to each funnel with stirring, and the funnels shaken for one minute. After the phases have separated, the organic layer is filtered through a dry filter and the optical density measured (the extract from the first funnel being used as reference solution). The results obtained are plotted within the coordinates optical density – Cu content (see diagram).

When the method described above was checked on a series of soils, plant material, and water by the method of additions, it was established that the error in determining copper does not exceed 5% (see Table 2).

In addition, a series of copper determinations was carried out on six samples of soil using nickel diethyldithiophosphate and using diphenylcarbazone by Lapin and Makarov's method [1]. It follows from the results obtained (Table 3) that results of copper determination by both methods are in reasonably good agreement, neverthless the agreement between two parallel determinations when nickel diethyldithiophosphate is used is somewhat better.

It should also be pointed out that determination of copper with nickel diethyldithiophosphate is considerably simpler and less tedious.

SUMMARY

A study has been made of the accuracy and reproducibility of the determination of copper in water, soils, and biological materials by A. I. Busev and M. I. Ivanyutin's method, using nickel diethyldithiophosphate as reagent. It has been shown that by using the reagent at a certain optimum concentration, and by removing interference from nitric acid, it is possible to reduce the error of the determination down to 5%. After the appropriate modifications have been made, the results obtained during the photometric determination of copper by means of nickel diethyldithiophosphate are superior in accuracy and reproducibility to those obtained by L. N. Lapin and V. P. Makarova's method, and at the same time are simpler and more rapid.

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*Low results are obtained if preliminary heating of the test water is omitted.

GRAVIMETRIC DETERMINATION OF SCANDIUM BY MEANS OF BENZENESELENINIC AND BENZENESULFINIC ACIDS

I. P. Alimarin and N. V. Shakhova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Of the organic reagents which precipitate scandium, the ones used are ammonium tartrate, oxalic acid, inositol-pyrophosphoric acid (phytic), alizarinsulfonic acid, and 8-hydroxyquinoline. The reactions with these reagents have been carefully studied by Fisher and Bock [1], and later by Vickery [2] using Sc^{46}. It was established that all these reagents suffer from some disadvantages. Accordingly, a search for new organic precipitants of scandium is a necessary prerequisite for the successful solution of problems in the preparative and analytical chemistry of scandium. We have studied ammonium benzeneseleninate and benzenesulfinate as possible reagents for this purpose.

Feigl [3] was the first to suggest benzeneseleninic acid as an analytical reagent, and it has been examined by Alimarin and Sotnikov [4].

We established that ammonium benzeneseleninate forms with scanadium in neutral and weakly acid solutions, a white crystalline precipitate which is readily soluble in mineral acids. Ammonia decomposes this compound with formation of the hydroxide. The sensitivity of the reaction is 5 μg/ml. X-ray studies of the precipitate confirmed its crystalline nature (Fig. 1). According to results of chemical analysis the scandium compound corresponds to the formula $Sc(C_6H_5SeO_2)_3$, the scandium content being 7.38%. Thsi compound can be recommended as a gravimetric form. A thermogravimetric study of the precipitate confirmed the stability of scandium benzeneseleninate at temperatures up to 120°. On heating to 600° this compound is completely converted into scandium oxide (Fig. 2).

Table 1. Determination of Scandium as Sc_2O_3

Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
		mg	%
1.23	1.20	+0.03	+2.4
1.29	1.18	+0.05	+4.0
2.46	2.49	+0.03	+1.2
2.46	2.50	+0.04	+1.6
5.90	5.82	−0.08	−1.3
5.90	5.93	+0.03	+0.1

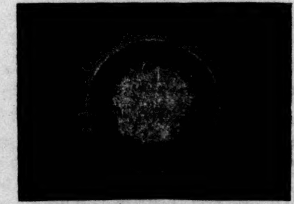

Fig. 1. X-ray spectrogram of scandium benzeneseleninate.

Benzeneseleninic acid has a number of advantages over organic reagents suggested earlier. Scandium benzeneseleninate has a low correction factor f = 0.0738, the precipitate is formed in a crystalline state in a short time (15 min), and it can be rapidly brought to constant weight by drying at 105°.

The difference in the solubility of scandium and zirconium benzeneseleninates (see [5]) has enabled us to develop a technique for determining scandium, and for separating it from zirconium.

A 20% solution of ammonium benzeneseleninate was prepared by dissolving the commercial reagent in distilled water. A scandium chloride solution was prepared by dissolving scandium oxide in redistilled concentrated hydrochloric acid on careful heating, with subsequent evaporation of the acid until the moist scandium chloride salt separated out; this was dissolved in distilled water. The concentration of the solution was establihsed by precipitation of scandium

TABLE 2 Determination of Scanduim by Weighing it as Scandium Benzeneseleninate

Wt. of Sc($C_6H_5SeO_2$)$_3$, mg	Sc taken, mg	Sc found, mg	Error		Wt. of Sc($C_6H_5SeO_2$)$_3$, mg	Sc taken, mg	Sc found, mg	Error	
			mg	%				mg	%
37,90	2,81	2,80	—0,01	—0,4	9,55	0,70	0,71	+0,01	+1,5
38,00	2,81	2,81	0,00	0,0	4,80	0,35	0,35	0.00	0,0
37,95	2.81	2,80	0,00	0,0	4,82	0,35	0,36	+0,01	+3,0
19,00	1,40	1,40	0,00	0,0	4,75	0,35	0,35	0,00	0,0
18,95	1,40	1,37	—0,03	—2,0	1,95	0,14	0,14	0,00	0,0
19,00	1,40	1,40	0,00	0,0	1,92	0,14	0,14	0,00	0,0
9,35	0,70	0,69	—0,01	—1,5	1,85	0,14	0,14	0,00	0,0
9,45	0,70	0,70	0,00	0,0					

TABLE 3. Separation of Scandium and Zirconium by Precipitation with Ammonium Benzeneseleninate and Using Zr^{95}

Sc : Zr	Sc_2O_3 taken, mg	Zr^{95} added cpm	Sc_2O_3 found mg	Zr^{95} found cpm	Error mg
1 : 1	1,24	1270	1,20	1263	—0,04
	2,49	1270	2,49	1257	0,00
1 : 2	1,24	1270	1,21	1245	—0,03
	2,49	1270	2,45	1269	—0,04
1 : 10	1,24	1270	1,22	1235	—0,02
	2,49	1270	2,52	1251	+0.03
	4,98	1270	5,06	.1274	+0,08

TABLE 4. Separation of Scandium and Zirconium by Precipitation with Ammonium Benzeneseleninate and Using Sc^{46}

Sc : Zr	Sc_2O_3 taken, mg	Sc^{46} added, cpm	Sc_2O_3 found, mg	Sc^{46} found cpm	Error mg
1 : 1	1,24	2,432	1,21	2367	—0,01
	2,49	1715	2,46	1704	—0,03
1 : 2	1,24	1933	1,19	1928	—0,05
	2,49	1920	2,50	1924	+0,01
1 : 10	1,24	2624	1,23	2240	—0,01
	2,49	2637	2,52	2250	+0,03

TABLE 5. Determination of Scandium by Precipitation with Ammonium Benzenesulfinate and Weighing as Sc_2O_3

Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
		mg	%
1,47	1,52	+0,05	+3,3
1,47	1,50	+0,03	+2,0
1,47	1,45	—0,02	—1,3
3,67	3,69	+0,02	+0,5
3,67	3,70	+0,03	+0,8
3,67	3,67	0,00	0,0
12,80	12,80	0,00	0,0
12,80	12,93	+0,11	+0,8
12,80	12,90	—0.10	—0,8

TABLE 6. Separation of Scandium and the Rare Earths by Precipitation with Ammonium Benzenesulfinate

Sc : Rare Earths	Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
			mg	%
1 : 1	2,37	2,20	—0,17	—7,7
	2,37	2,18	—0,19	—8,6
1 : 10	2,37	2,35	—0,02	—0,8
	2,37	2,32	—0,05	—2,1
1 : 20	2,37	2,36	—0,01	—0,4
	2,37	2,37	0,00	0,0
	4,74	4,70	—0,04	—0,8
1 : 50	2,37	2,35	—0,02	—0,8
	2,37	2,37	0,00	0,0
	4,74	4,77	+0,03	+0,6

hydroxide, and complexometric titration in the presence of murexide. Zirconyl oxychloride was dissolved in distilled water and the concentration of the solution established complexometrically.

Completeness of precipitation, and the purity of the precipitates obtained were checked radiometrically using the isotopes Sc^{46} and Zr^{95}. The latter was freed from the daughter element niobium by repeated coprecipitation of Nb^{95} with MnO_2. Sc^{46} was obtained by bombarding scandium oxide with neutrons by the reaction Sc^{45} (n, γ) Sc^{46}.

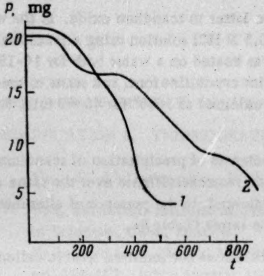

Fig. 2. Thermogravigrams of scandium benzeneseleninate (1) and scandium benzenesulfinate (2).

Scandium benzeneseleninate was precipitated from weakly acid solutions, 50 ml of a solution of the scandium salt was heated on a water bath, a drop of methyl orange was added and the solution neutralized with ammonia solution (1:1) to the first color change of the indicator. Five ml of ammonium benzeneseleninate solution (precipitate concentration 2% by volume) was added to the hot solution, and the mixture cooled to room temperature. Under these conditions the precipitate of scandium benzeneseleninate packed together and the solution above the precipitate clarified. Subsequently scandium can be determined either by weighing the precipitate of scandium benzeneseleninate or by calcining the latter to the oxide. To obtain the oxide the precipitate was filtered off through a paper filter and calcined at 800° for 30 min (Table 1).

For determination of scandium as the benzeneseleninate, the precipitate obtained as described above was filtered off through a glass microfilter with a No. 4 porous glass bottom, the precipitate was washed with 10-15 ml of twice distilled water and then with the same amount of ethanol; it was finally dried at 105° for 20 min (Table 2).

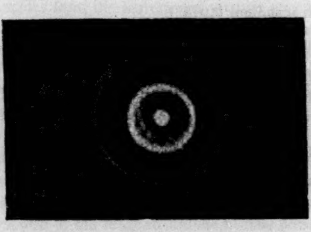

Fig. 3. X-ray spectrogram of scandium benzenesulfinate.

In order to separate scandium from zirconium the latter was precipitated from hot 1 N HCl solution with ammonium benzeneseleninate, the precipitate was filtered through a blue band filter paper, and carefully washed with 0.5% ammonium benzeneseleninate solution. The filtrate was evaporated on a water bath to a volume of 50 ml, and scandium determined by one of the methods indicated above.

Completeness of separation of scandium from zirconium was checked by means of radioactive indicators. Two series of experiments were carried out. In the first series of experiments completeness of precipitation of zirconium in the presence of scandium was controlled by means of Zr^{95}; the scandium was determined by calcining scandium benzeneseleninate to scandium oxide (Table 3). In the second series of experiments completeness of precipitation of scandium was checked by means of Sc^{46} (Table 4).

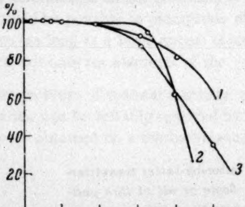

Fig. 4. Precipitation of scandium (I), zirconium (II), and thorium (III) by ammonium benzenesulfinate as a function of the acidity.

Scandium was quantitatively separated from zirconium at a maximum ratio of Sc:Zr = 1:10; at higher zirconium concentrations high results were obtained for scandium.

Ammonium benzenesulfinate has been used by Alimarin and Alikberov for the determination of zirconium and thorium [6, 7]. With scandium, in acid (down to 2.5 N) and neutral solutions, benzenesulfinic acid, and its sodium and ammonium salts form a white flocculent precipitate which is soluble in mineral acids. The sensitivity of the reaction is 2 μg/ml. X-ray studies (Fig. 3) showed that the precipitate formed has a crystalline structure. It should be pointed out that the acidity of the solution strongly affects the structure of the precipitate formed; thus in acid solutions (from 0.3 N upward) a finely crystalline precipitate is formed which is difficult to filter, while scandium benzenesulfinate formed in neutral solutions is compact and is readily filtered. A study of the compound formed confirmed that it is a normal salt with the composition $Sc(C_6H_5SO_2)_3 \cdot xH_2O$. Scandium benzenesulfinate cannot be recommended as a gravimetric form because of its variable water content. It is clear from the thermogravigram of scandium benzenesulfinate (Fig. 2) that the latter is completely converted into scandium oxide at temperatures above 800°. We have developed a method for separating scandium from the rare earths, iron, and aluminum, and for determining it by precipitation as scandium benzenesulfinate, followed by calcination of the latter to scandium oxide. In the work described here scandium benzenesulfinate was precipitated from 50 ml of a 0.5 N HCl solution using a precipitant concentration of 1% by volume. After addition of precipitant the solution was heated on a water bath for 10-15 min. Heating above 80° should be avoided, since the precipitate separates out in a fine crystalline form and starts to creep up the vessel walls. The precipitate was filtered through a blue band filter and calcined at 1000° for 45-60 min. Scandium was determined by weighing it as its oxide (Table 5).

A study was made of the effect of the acidity of the medium on completeness of precipitation of scandium. It is clear from Fig. 4 that zirconium and thorium are precipitated by ammonium benzenesulfinate over the same acidity range as scandium. Precipitation of scandium, according to the technique indicated, in the presence of aluminum and the yttrium group of the rare earths permits scandium to be separated from the latter (Table 6).

The presence of less than 5 mg of iron in 50 ml of a solution in 0.7 N HCl does not interfere with scandium determination.

SUMMARY

Benzeneseleninic acid and its ammonium salt form a white crystalline precipitate with scandium in neutral and weakly acid solutions. The composition of the compound corresponds to the formula $Sc(C_6H_5SeO_2)_3$. The precipitate can be recommended as a gravimetric form (conversion factor to scandium 0.0738).

A method has been developed for the determination of scandium in the presence of the rare earths, iron, and aluminum by precipitating it with benzensulfinic acid. The composition of the precipitate approximates to the formula $Sc(C_6H_5SO_2)_3 \cdot xH_2O$. For quantitative determination of scandium this compound is calcined at 1000° and the scandium is weighed as Sc_2O_3.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THERMOGRAVIMETRY IN ANALYTICAL CHEMISTRY

COMMUNICATION 3. THERMOGRAVIMETRIC STUDY OF LANTHANUM CARBONATE

Yu. S. Sklyarenko, I. S. Sklyarenko, and T. M. Chubukova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy
of Sciences, USSR, Moscow

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Carbonate ions have been used for a long time in preparative practice, both for coarse separation of total lanthanides from the cerium and yttrium groups [1, 2], and also for the preparation of individual rare earth elements [3-5]. The normal carbonates of the rare earths can be prepared by different methods – by passing CO_2 into a suspension of hydroxides [6], by hydrolysis of solutions of their trichloroacetates [7], and, finally, by the interaction of readily soluble salts with the alkali metal carbonates. The last method is certainly the simplest and most practicable; there is, however, no unanimous opinion regarding the composition of the sparingly soluble compounds formed in this case. The precipitates formed have been ascribed the structure of basic carbonates [8], double salts [9], or normal carbonates [10]. On the basis of our own results on the chemical analysis of lanthanum, neodymium, erbium, and yttrium carbonates [11, 12] prepared by the last method, and also on the basis of a study of the system alkali metal carbonate – trivalent cerium – water, carried out by physicochemical analytical methods [13], we are of the opinion that normal carbonates with the composition $R_2(CO_3)_3 \cdot nH_2O$ are formed over the concentration range studied when equimolar amounts of the reagents are used. The possibility of using these compounds for anlytical purposes, and, in particular, as a gravimetric form, has not apparently been examined.

No strictly quantitative results on the solubility of the lanthanide carbonates has been published. Nevertheless, tentative information on the solubility of lanthanum and neodymium carbonates [11, 12] gives ground for assuming that it should be possible to precipitate the elements of the cerium group quantitatively by means of alkali metal carbonates (as long as a large excess of precipitant is avoided, since the latter at high concentrations act as complexing agents not only for elements of the yttrium group, but also for cerium group elements).

The problem of thermal stability, particularly with respect to establishing the range over which a particular compound exists, can be reliably resolved by Duval's thermogravimetric method [14]. The results given in the present article were obtained on a thermobalance of simplified construction described previously [15, 16].

EXPERIMENTAL

X-ray structural analysis showed that the lanthanum oxide used in the present work contained 0.15% each of Pr_6O_{11} and Nd_2O_3. Other rare earths present as impurities could not be detected. Of other foreign elements only about 0.01% iron could be found. Potassium, sodium, and ammonium carbonates – chemically pure grade – were used without further purification. Chemicallly pure grade hydrochloric acid was redistilled. 1, 0.1, and 0.01 N solutions of $LaCl_3$ were prepared from accurately weighed amounts of La_2O_3. The concentration of the solutions was checked gravimetrically by precipitation with oxalic acid. The concentration of the solutions of the alkali carbonates (1, 0.1, and 0.01 N) was determined by titration with hydrochloric acid.

Equal volumes of lanthanum chloride solution and alkali metal carbonate solution of the same normality were mixed at room temperature and allowed to stand for two hours, after which the precipitates formed were filtered off. Subsequent treatment of the precipitates to prepare them for thermogravimetric study differed slightly in detail. Aliquots of 30 to 50 mg of the treated precipitates were used for thermal decomposition. The experimental procedure was completely identical to that described previously [15, 16].

• For communication 2, see Zh. analit. khimii 15, 706 (1960)

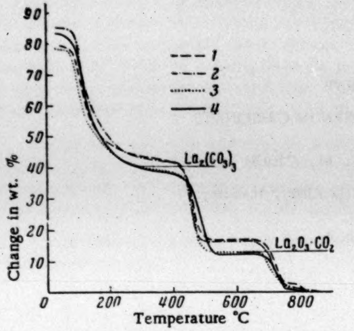

Fig. 1. Thermogravigrams of lanthanum carbonate precipitated with potassium carbonate of varying concentration. 1) From 1 N $LaCl_3$; 2) from 0.1 N $LaCl_3$; 3) from 0.01 N $LaCl_3$; 4) from 1 N $LaCl_3$, precipitate washed with water.

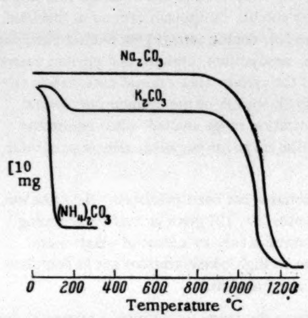

Fig. 2. Thermogravigrams of alkali metal carbonates.

It is fairly frequently stated in the literature [8] that there is a relationship between the composition of the precipitates formed in the systems rare earth^{3+} – Me_2CO_3 – H_2O (where Me is the alkali metal cation) and the concentration of the original solutions. It was necessary therefore to establish whether there is such a relationship, and if there is, to what extent this factor affects the nature of the thermogravigrams obtained. Moreover, it was also necessary to define more accurately the method of preparing the sample for study. In Fig. 1 are shown thermogravigrams of carbonate precipitates obtained by precipitation of lanthanum chloride with potassium carbonate at room temperature. Curves 1, 2, and 3 correspond to precipitates obtained by precipitation from 1, 0.1, and 0.01 N solutions and filtered off by means of a water pump, without washing. Curve 4 corresponds to the precipitate obtained from a 1 N solution, but carefully washed on the filter with water.

As Fig. 1 shows the general nature of all four thermogravigrams, after the sharp drop in the curve determined by removal of water of crystallization and hygroscopic water from the precipitate, is the same; over the range 275-400° there is an almost horizontal part corresponding, according to calculation, to the anhydrous carbonate $La_2(CO_3)_3$. This is followed by another sharp drop determined by the decomposition of the anhydrous carbonate, and a distinct area (from 500 to 650°) corresponding to the existence of its intermediate decomposition product. Calculation in this case indicates that this product has the approximate formula $La_2O_3 \cdot CO_2$. The third drop on the curve corresponds to decomposition of this compound and terminates at a temperature slightly higher than 800°. Starting from this temperature only lanthanum oxide La_2O_3 is thermally stable. There are, nevertheless, certain differences which exceed the normal errors met in thermogravimetric analysis. On the one hand, curves 1 and 2, which correspond to the more concentrated solutions, throughout their whole length lie above curve 3, which corresponds to the most dilute of the solutions used. On the other hand, curve 2 lies above curve 4, although the solutions in both cases are the same, the difference being in the preparation of the precipitates for analysis (washing).

It would appear that the simplest explanation of both these facts is hydrolysis. Actually, in the first case one could assume a higher degree of hydrolysis of the carbonate compounds obtained from the most dilute original solutions, and in the second hydrolysis of the precipitate during washing with water. One objection to this hypothesis, however, in the first place, is the thermogravigram of the precipitate obtained from 0.01 N solutions heated beforehand to 60-70°. This curve is not included in Fig. 1 since it coincides completely with curve 3. If hydrolysis had actually occured then the extent of hydrolyis of the precipitates obtained from hot solutions would be greater, and the curve mentioned above would lie below curve 3. In the second place, only the deviations on the initial parts of the thermogravigrams can be explained by hydrolysis, since there is only a very small probability that the hydrolyzed compounds can exist at very high temperatures, e.g., over the range within which the intermediate compound is stable. At the same time deviations between the curves are observed over this range too.

Another possible interpretation of the phenomena observed is the difference in the degree of entrainment by the precipitates of the reaction products (KCl) from the mother liquors when original solutions of varying concentrations are used. In fact, after removal of water from the precipitates, the KCl entrained by the precipitates remains, and is only removed at very high temperatures. All the precipitates were treated under identical conditions; accordingly their moisture content is approximately the same, and the amount of salt (KCl) remaining in the precipitate should be proportional to its concentration in the mother liquor. If stoichiometric proportions are strictly observed, the initial products cannot be present in the solutions, and consequently in the precipitates; if, however, the process is used for actual precipitation of lanthanum carbonate or the carbonates of other elements of the cerium group, then naturally a certain excess of the alkali metal carbonate will be present in solution, and also in the precipitate. Bearing this in mind, the thermogravigrams of the three most readily available precipitants – sodium, potassium, and ammonium carbonates – are shown in Fig. 2.

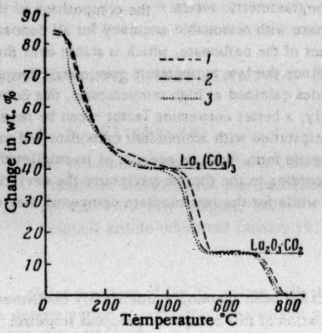

Fig. 3. Thermogravigrams of lanthanum carbonate precipitated by ammonium carbonate from solutions of varying initial concentration. 1) From 1 N $LaCl_3$; 2) from 0.1 N $LaCl_3$; 3) from 0.01 N $LaCl_3$.

The results of thermogravimetric analysis, as well as published information [17] on the thermal stability of the carbonates and chlorides of potassium, sodium, and ammonium indicate that ammonium carbonate should be chosen as the precipitant, since the presence of ammonium cabonate itself or of ammonium choride should not affect the composition of the gravimetric form of the anhydrous carbonates, and, in particular, that of the intermediate product obtained during the thermal decomposition of the anhydrous carbonate. The next series of experiments was carried out with ammonium carbonate. The method used was left unchanged, apart from the fact that the carbonate precipitates, after having been filtered, were dried in a vacuum desiccator to constant weight. The corresponding thermogravigrams are shown in Fig. 3. Curves 1, 2, and 3 correspond to the precipitates obtained from 1, 0.1, and 0.01 N solutions respectively.

From these results it is clear that the modifications made to the original method enable better results to be obtained. Accordingly, the main factor affecting the composition of the carbonate precipitates would appear to be contamination of these precipitates by the alkali metal chloride, and not differences in the extent of hydrolysis as a function of the concentration of the original solutions. On washing the precipitates for a long time with water, hydrolysis, apparently, also takes place (this is clear from a comparison of curve 4, Fig. 1 and Curve 1, Fig. 3); its effect is, however, small. The series of experiments also enabled us to define the temperature range over which both compounds are stable more accurately; this range is about 100° (300-400°) for anhydrous lanthanum carbonate; for the decomposition product of the latter this range is slightly wider 550-675°, the section of the curve over this range being completely horizontal. In order to confirm the composition of both compounds, the precipitates were kept at constant weight at temperatures corresponding approximately to the middle of the horizontal sections (375 and 600°), and analyzed [18]. Results of elemental analysis of both products obtained from original solutions with concentrations ranging from 1 to 0.01 N are given in Tables 1 and 2.

Table 1. Elemental Analysis of the Compound Brought to Constant Weight at 375° [Suggested composition – $La_2(CO)_3$]

Test Element*	Calculated, %	Found on precipit. from sol. of varying normality, %		
		1 N	0,1 N	0,01 N
C	7,86	7,67	7,75	7,90
O	31,44	31,56	31,25	31,20
La_2O_3	71,17	71,20	71,60	71,10
CO_2/La_2O_3	3,0	2,93	2,98	3,01

*Hydrogen was not detected in any of the forms; oxygen was determined by difference.

Table 2. Elemental Analysis of the Compound Brought to Constant Weight at 600° (suggested composition $La_2O_3 \cdot CO_2$)

Test Element*	Calculated, %	Found on precipit. from sol. of varying normality, %		
		1 N	0,1 N	0,01 N
C	3,35	3,23	3,30	3,13
O	21,60	22,97	23,80	21,07
La_2O_3	88,00	86,6	85,5	88,0
CO_2/La_2O_3	1,0	1,02	1,05	0,96

*Hydrogen was not detected in any of the forms; oxygen was determined by difference.

It is clear that the results of chemical analysis confirm the thermogravimetric results – the composition of the precipitates at 375° corresponds to the formula for the anhydrous carbonate with reasonable accuracy for all concentrations of the initial solutions used. The thermal decomposition product of the carbonate, which is stable over the range 550-675°, corresponds to the approximate formula $La_2O_3 \cdot CO_2$. Since the low temperature gravimetric forms of the rare earths are usually more readily soluble in acids than the oxides calcined at high temperatures, this compound, which, moreover, has a slightly higher weight – and, accordingly, a better conversion factor – can be recommended as a gravimetric form for the determination of lanthanum (precipitation with ammonium carbonate and calcination at 600°). The anhydrous carbonate is less suitable as a gravimetric form, both on account of its smaller thermal stability range, and because of a lower experimental accuracy (according to the thermogravigrams the deviations from the theroretical composition for the anyhdrous carbonate is 3-5%, while for the intermediate compound they do not exceed 1%).

SUMMARY

Formation of the normal carbonate of lanthanum $La_2(CO_3)_3 \cdot nH_2O$ has been thermogravimetrically confirmed in the system $LaCl_3 - Me_2CO_3$ ($Me = K^+, NH_4^+$) $- H_2O$. Thermal dissociation of this compound proceeds stepwise: $La_2(CO_3)_3 \cdot nH_2O \rightarrow La_2(CO_3)_3 \rightarrow La_2O_3 \cdot CO_2 \rightarrow La_2O_3$.

The thermal stability ranges of $La_2(CO_3)_3$ (300-400°) and $La_2O_3 \cdot CO_2$ (550-675°) have been determined.

The compound $La_2O_3 \cdot CO_2$ is recommended as a gravimetric form for the determination of lanthanum. Ammonium carbonate is the most suitable precipitant, while the calcination temperature is 600°.

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PHOTOMETRIC DETERMINATION OF GALLIUM WITH BUTYLRHODAMINE B

L. M. Skrebkova

M. V. Lomonosov Moscow State University

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Color reactions of $GaCl_4^-$ anions with the cation of basic organic dyes have acquired exceptional importance for the determination of microgram amounts of gallium; of these dyes the one which has found widest application is rhodamine B (or C) [1-6].

Rhodamine B contains an organic cation of large size. The presence of a carboxyl group in the rhodamine B molecule weakens to some extent the basic properties of this cation, and increases the solubility of the salts formed by rhodamine B.

Kuznetsov and Bol'shakova [7] have shown that completeness of precipitation, coprecipitation, and extraction of the elements can be appreciably increased if, instead of rhodamine B, one of its esters, e.g., the butyl ester of rhodamine B, so-called butylrhodamine B is used.

We have adopted butylrhodamine B for the photometric determination of gallium.

EXPERIMENTAL

The following reagents were used:

1. A 0.1% solution of butylrhodamine B in 6 N hydrochloric acid. The reagent was synthesized by Kuznetsov and Bol'skakova's method [7].

2. Gallium solution containing 1 mg gallium per ml of 6 N hydrochloric acid. The solution was prepared by dissolving an accurately weighed aliquot of spectrographically pure gallium metal in aqua regia; nitric acid was removed by a double evaporation with concentrated hydrochloric acid. The dry residue was dissolved in 6 N HCl. Working soolutions of gallium containing 10, 1.0, 0.1 μg of gallium per ml were prepared by diluting the stock solution with 6 N HCl.

3. A 20% solution of titanium trichloride in 6 N HCl. The solution was prepared by dissolving titanium metal in hydrochloric acid.

The optical density was measured on a SF-4 spectrophotometer and on a FÉK-N photocolorimeter-nephelometer.

Butylrhodamine B is a dark-raspberry, crystalline material which is soluble in water, ethanol, and acetone; it is insoluble in benzene and toluene. A hydrochloric acid solution of butylrhodamine B has an orange-red color. Butylrhodamine B is hardly extracted at all from aqueous solutions by benzene, toluene, and chloroform.

In hydrochloric acid solution butylrhodamine B interacts with gallium to form a compound which can be extracted with benzene, and toluene, the extract obtained being rose-violet in color.

A toluene solution of butylrhodamine B chlorogallate has an absorption maximum at 565 mμ; at this wavelength the reagent itself hardly absorbs any light (Fig. 1).

One of the drawbacks of the rhodamine photometric determination of gallium by Onischi's method is the comparatively low extent to which the rhodamine B chlorogallate is extracted with benzene. Several authors have tried to improve Onischi's rhodamine method, and have recommended substitution of benzene by a mixture of benzene and ether [4], a mixture of chlorobenzene and CCl_4 [3], or a mixture of benzene and butyl acetate [5].

Butylrhodamine B is equally well extracted by benzene, toluene, and the mixed extractants mentioned above, so that there is no need to use the mixtures (Table 1).

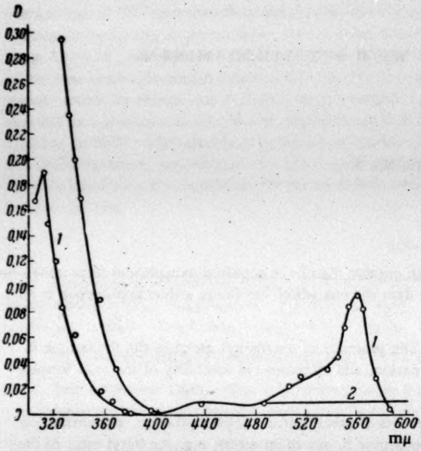

Fig. 1. Absorption curves. 1) Toluene extract of butylrhodamine B chlorogallate; 2) toluene extract of butylrhodamine B.

Table 1. Extraction of Butylrhodamine B Chlorogallate with Various Solvents

Solvent	Optical density		
	Blank	Test containing 0.4 μg Ga/ml	Difference
Benzene	0.009	0.410	0.401
Toluene	0.01	0.420	0.410
Benzene + ether (10 : 1)	0.013	0.425	0.412
Benzene + amyl acetate (4 : 1)	0.015	0.430	0.415

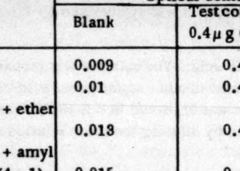

Fig. 2. Effect of hydrochloric acid concentration on extraction: 1) Butylrhodamine B chlorogallate with toluene (reference solution, the blank solution); 2) butylrhodamine B with toluene (reference solution, toluene.

A single extraction is sufficient to ensure almost complete extraction of butylrhodamine B chlorogallate by the solvents mentioned.

The sensitivity of the reaction of gallium with butylrhodamine B is almost one order higher than the reaction with rhodamine B. The limit of identification is 0.005 μg gallium in 1 ml of solution.

The molar extinction coefficient of butylrhodamine B chlorogallate is 90,000, while the molar extinction coefficient of rhodamine B chlorogallate determined by Onischi and Sandell [2] is 60,000.

Extraction of butylrhodamine B chlorogallate with toluene (benzene) depends on the acidity of the solution; the optimum acidity lies within the range 6 to 6.5 N HCl (Fig. 2).

It is interesting to note that extraction of the reagent itself becomes appreciable at low acidities of the solution,but there is hardly any extraction starting from 5 N HCl.

Colored solutions of butylrhodamine B chlorogallate conform to Beer's law over a wide gallium concentration range (0.005-2 μg/ml). Fig.3 shows a calibration curve for a narrow concentration range (0.1-1 μg Ga in 1 ml of solution). The optical density was measured both on a spectrophotometer at 565 mμ, and also on a FÉK-N apparatus fitted with a 6-M filter, having maximum light transmission at 584 mμ; a 1 cm cell was used. Reference solutions were prepared by shaking hydrochloric acid solutions containing the same amounts of butylrhodamine B and titanium trichloride with toluene.

The elements which interfere with the determination of gallium by means of buytlrhodamine B are those elements which also interfere with determination of gallium with rhodamine B, i.e. Au^{III}, Fe^{III}, Sb^{V}, and Tl^{III}. The influence of these cations can be eliminated by adding titanium trichloride as a reducing agent to the test solution. In those cases where commercial hydrochloric acid, which usually contains traces of iron, is used, titanium trichloride must be added even when working with pure gallium solutions because of the high sensitivity of the reaction of butylrhodamine B with ferric iron (rhodamine B is less sensitive to iron).

Where test materials contain large amounts of aluminum (> 0.3 mg) gallium must be separated beforehand from aluminum. Extraction of gallium from 6 N HCl with ether, butyl or amyl acetate can be used for this purpose.

When test materials contain high contents of interfering elements it is always better to carry out a preliminary extraction of gallium in order to get reliable results.

Table 2. Determination of Gallium in Standard Samples

Samples	Ga% Present	Ga% Found
Copper-zinc ore	0.0012	0.0012
Unroasted lead dust	0.0001	0.00009
Bauxite No. 1	0.0065	0.0069
Bauxite No. 2	0.0044	0.0042
Quartz-topaz greisens:		
No. 1	0.0020	0.0021
No. 2	0.0005	0.0005
No. 3	0.0003	0.00035

Gallium was determined by means of butylrhodamine B in a large number of different gallium-containing materials: unroasted lead dust, bauxities, copper-zinc ores, and quartz-topaz greisens.

Analytical Procedure. An aliquot of test material weighing from 0.1 to 0.5 g (depending on the gallium content) is fused in a corundum crucible with 1-1.5 g of Na_2O_2 and 0.5 g of NaOH at 600-650°. The melt is leached with hot water, the precipitate of hydroxides is dissolved in hydrochloric acid and the hydrochloric solution evaporated on a water bath until the dry salts are obtained. The salts are dissolved in 6 N hydrochloric acid and the solution transferred to a separating funnel.

Gallium is extracted three times with amyl acetate in the presence of a reducing agent − titanium trichloride; the funnel is shaken for 1.5-2 min each time.

The extract is washed three times with 6N HCl and the gallium reextracted three times with water. The aqueous solutions obtained are evaporated on a water bath until the dry salts are obtained, the latter are dissolved in 5 ml of 6 N HCl and transferred to a 25 ml separating funnel; the porcelain base used for the evaporation is rinsed with 2 ml of 6 N HCl. Two ml of 20% titanium trichloride solution is added to the separating funnel, the latter is shaken and 1 ml of 0.1% butylrhodamine solution added. Butylrhodamine B chlorogallate is then extracted with 10 ml of toluene (benzene) by shaking for 2 min. After the phases have separated out the aqueous solution is drained off, while the extract is filtered through a plug of glass wool to free it from drops of water; the first portion of filtrate is rejected, while the remainder is collected in a 1 cm cell.

The optical density is measured on a SF-4 spectrophotometer at 565 mμ or on a FĚK-N apparatus.

The amount of gallium is determined from the calibration curve.

Results for the determination of gallium in different materials are given in Table 2.

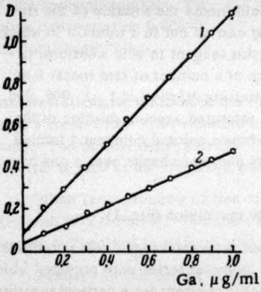

Fig. 3. Calibration lines for determination of gallium with butylrhodamine B on: 1) SF-4 spectrophotometer at 565 mμ; 2) FĚK-N photocolorimeter − nephelometer.

SUMMARY

The formation of a complex between $GaCl_4^-$ anions and butylrhodamine B, and the extraction of this complex (butylrhodamine B chlorogallate) with toluene (benzene) have been studied. It has been shown that this reaction is significantly more sensitive than the well known reaction with rhodamine B.

A method has been developed for the photometric determination of gallium with butylrhodamine B in various gallium-containing materials.

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PHOTOMETRIC DETERMINATION OF TITANIUM WITH 2-(α-N-PIPERIDINO) ISOPROPYL-4-HYDROXYTETRAHYDROFURAN-3-ONE

O. R. Skorokhod, I. G. Tishchenko, and I. N. Volneiko

V. I. Lenin Belorussian State University, Minsk

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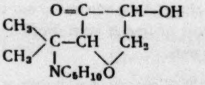
In acid media quadrivalent titanium forms soluble colored compounds [1] with certain susbtituted tetrahydrofuranones prepared in recent years by Nazarov et al [2].

We thought that it would be interesting to study the interaction of quadrivalent titanium ions with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one as a representative of the substituted tetrahydrofuranones, with the idea of establishing the possibility of using it for the determination of titanium.

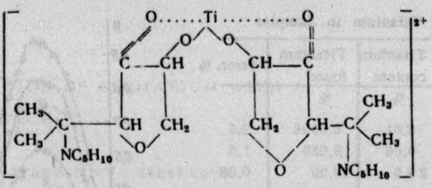


In acid solution (pH < 2) quadrivalent titanium forms with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one a soluble compound with an intense red-brown color, which is not destroyed in strong acids and in the presence of sulfates, oxalates, phosphates, borates, and other anions. In strongly acid media the solution of the titanium compound acquires a red-violet and even a blue color. The reaction is best carried out in a solution in which the hydrogen ion concentration is approximately equal to 1 g-equiv/liter. Using this reagent in acid solutions, titanium can be detected in the presence of all Group I-V cations, and in the presence of a number of rare metal ions: Li^+, Be^{2+}, Zr^{IV}, Ce^{IV}, VO_3^-. The sensitivity of detection is characterized by a limiting dilution of 1 : 1, 000, 000. The compound formed is farily stable. The red-brown color obtained on adding a saturated aqueous solution of the reagent is preserved without change for 20 min after mixing the solutions; the red-brown colored compound formed when an alcoholic solution of the reagent is used is more stable; the optical density does not change over a one hour period.

The maximum absorption of solutions of the compound formed lies in the 420 mμ region (Fig. 1).

The molar ration which obtains during the interaction of quadrivalent titanium with the raegent was determined by the isomolar series method and by the equilibrium shift method [3, 4]. Several isomolar series were prepared which differed in their total concentration of reactants, the hydrogen ion concentration being constant for a particular series. The optical density was measured on a FÉK-M photoelectriccolorimeter using a path length of 1.035. The titanium and reagent concentration was varied over the range 0.00398-0.038 M, while that of the acid was varied between 0.04-1.9 g-equiv/liter. As the results obtained show (Fig. 2), the optical density is a maximum when the ratio of the components Ti : R = 1 : 2. The same ratio was obtained on using the equilibrium shift method, in which the optical density of solutions with a constant concentration of titanium and variable concentrations of the reagent was measured, the reagent concentration being varied over a wide range.

By means of electrophoresis (voltage 60-70 v) and ion exchange resins (sulfocoal in the H-form, and the resin ÉDÉ-10 in the OH-form) it was established that the titanium in the colored compound is found in the form of a cation. It should be pointed out that a complex with a ratio Ti : R = 1 : 2 is formed in acid solutions, in which as is known [1], the reagent exists as the keto-form. Taking all this into account, the following probable structure can be advanced for the compound formed:



Dilute solutions of the titanium compound formed (concentration 0.0020 M and lower) conform to Beer's law.

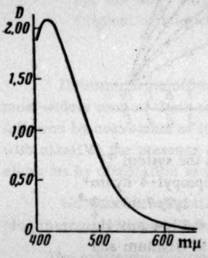


Fig. 1. Absorption spectrum of solutions of the compound of quadrivalent titanium with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one. SF-2M spectrohotograph. Titanium concentration 0.00045 M. Path length 5 mm.

We have used the formation of a colored, soluble compound of titanium with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one as the basis of a photometric method of determining titanium. As indicated above, none of the cations of Groups I – V, nor some rare metals, interfere with the qualitative detection of titanium.

Large amounts of trivalent iron interfere with titanium determination by increasing the color intensity of the solution. Neverthess a tenfold excess of iron with respect to titanium does not interfere with determination of the latter. (Table 1).

Nickel and cobalt, even when present in large amounts, do not interfere with titanium determination (the original solution is used as the reference solution).

Sodium ethylenediaminetetracetate (EDTA-Na) does not affect formation of the compound of quadrivalent titanium with the reagent, and does not interfere with titanium determination.

Titanium Determination. The material whose titanium content is to be determined is dissolved in about 2 N sulfuric acid (where necessary it is fused with $KHSO_4$ and then dissolved), the amount taken being such that a solution with a titanium concentration not greater than 0.0020 M is obtained. 5-6 drops of a saturated alcoholic solution of the reagent is added to 5 ml of the solution obtained, and the optical desnity measured using a green filter. The titanium content of the sample is determined from a calibration curve (constructed beforehand). The optical density can be measured within one hour of mixing the solutions. The original solution of test material is used as the reference solution.

When large amounts of iron are present, the titanium must be separated. Titanium does not form a stable complex with EDTA-Na [5]. Titanium is precipitated from solution with ammonia after addition of EDTA-Na, the precipitate is dissolved in sulfuric acid and the titanium determined as described above.

Results for the determination of titanium in several alloys ("standard samples") and minerals are given in Table 2.

TABLE 1. Effect of Accompanying Elements on the Optical Density of Solutions of the Titanium Compound

Titanium content, mg/liter	Impurity, g/liter			Optical density, λ=530mμ	Titanium content, mg/liter	Impurity, g/liter			Optical density λ=530mμ
	Fe^{III}	Co^{II}	Ni^{II}			Fe^{III}	Co^{II}	Ni^{II}	
42,6	—	—	—	0,21	85,3	—	18,4	—	0,37
42,6	0,45	—	—	0,21	85,3	—	27,6	—	0,37
42,6	0,89	—	—	0,23	85,3	—	55,2	—	0,38
42,6	1,34	—	—	0,24	85,3	—	—	56,2	0,37
85,3	—	—	—	0,37	85,3	—	—	84,2	0,37

Table 2. Determination of Titanium in Samples

Test Sample	Titanium content %	Titanium found %	Error, %
Instrument steel (EI 184)	0.01	0.0098	2.0
Steel (EI 274)	0.06	0.059	1.5
Ferrotitanium	29.0	28.99	0.03
Ilmenorutile mineral	53.04	52.96	0.15

Thus titanium can be determined with a reasonable degree of accuracy in alloys and minerals by means of 2-(α-N-piperidino)isopropyl-4-hydroxytetrahydrofuran-3-one.

SUMMARY

Quadrivalent titanium ions interact with 2-(α-N-piperidino) isopropyl-4-tetrahydrofuran-3-one to form a soluble compound with a red-brown color. The maximum absorption of solutions of the compound formed lies at 420 mμ; solutions of the complex conform to Beer's law.

A photometric method has been developed for the determination of titanium by means of 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one.

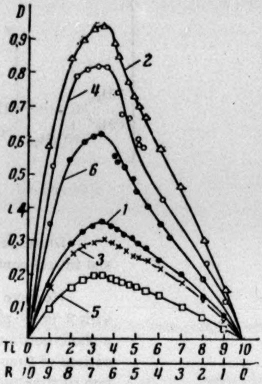


Fig. 2. Isomolar series in the system Ti^{IV} – 2-(α-N-piperidion) isopropyl-4-hydroxytetrahydrofuran-3-one. 1,2) 7.96×10^{-3} M titanium and reagent, 0.16g-equiv H$^+$ per liter; 3,4) 7.96×10^{-3} M titanium and reagent, 0.5 g-equiv H$^+$/liter; 5, 6) 3.98×10^{-3} M titanium and reagent, 0.16 g-equiv H$^+$/liter (1, 3, 5 at 530 mμ; 2, 4 6 at 400 mμ).

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AMPEROMETRIC TITRATION OF GERMANIUM WITH A SOLUTION OF PYROCATECHOL

A. I. Zelyanskaya and N. V. Stashkova

Institute of Metallurgy, Academy of Sciences, USSR, Ural Branch,
Sverdlovsk

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Determination of large amounts of germanium is carried out mainly by chemical methods at present. The most widely used of these methods is the gravimetric one based on precipitation of germanium with hydrogen sulfide, followed by conversion of its sulfide into the oxide [1]. The titrimetric method consists in titrating germanic acid with alkali in the presence of mannitol or glucose. When this method is used, germanium is separated from other elements by distillation as germanium chloride or by precipitation with hydrogen sulfide [2, 3].

We have developed a method for the amperometric titration of germanium with a pyrocatechol, using a dropping mercury electrode in an electrolyzer provided with an external anode.

The reference electrode was a saturated calomel electrode which was connected to the electrolyzer via an agar-agar bridge.

Titration was carried out with a 0.1 M solution of pyrocatechol measured out from a microburet with 0.01 mm scale division. A borate-acetate buffer with a pH 7-9 (0.2 M CH_3COONa + 0.05 M $Na_2B_4O_7$) proved to be the most suitable supporting electrolyte for titration. In contrast to the acetate supporting electrolyte we described earlier [4], the borate-acetate buffer permits one to obtain a clearly defined germanium wave at high concentrations of the latter in solution (8-10 mM/liter). Under these conditions a linear relation is observed between germanium concentration and its wave height. The half-wave potential of germanium under these conditions is −1.45 to −1.47 v; the limiting current can be measured at potentials of −1.6 to −1.8 v.

We established that addition of pyrocatechol leads to a decrease, and when a small excess has been added, to the disappearance of the germanium wave. Pyrocatechol itself, over the pH range in which germanium is polarographed, does not give a wave (Figs. 1 and 2).

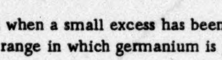
Titration of solutions with different germanium concentrations at −1.7 v showed that the molar ratio of pyrocatechol and germanium is constant as long as the germanium concentration of the solution being titrated is not less than 4mM/liter.

TABLE 1

Germanium concentration, mM/liter	No. of moles of pyrocatechol per mole of germanium
0.1	26.5
0.2	20.0
1	5.0
2	4.1
3	3.7
4	2.9
6	3.1
8	3.0

When this condition is observed three moles of pyrocatechol interact with one mole of germanium; this might possibly indicate formation of a complex with a coordination number of p = 3.

On the basis of these experimental results, and by analogy with the known pyrocatechol complexes of Si, Ti, Fe, etc [5-7], it may be postulated that the following complex ion is present in solution:



The absence of a germanium wave in the presence of excess pyrocatechol, i.e. the wave is shifted by not less than −0.5 v, indicates that the complex formed possesses high stability.

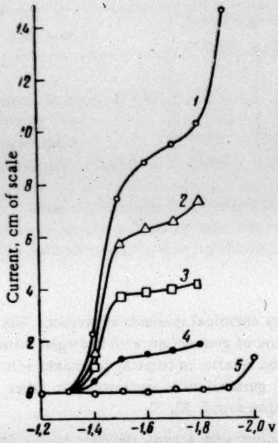


Fig. 1. Germanium polarograms (0.06 mM in 10 ml) in a supporting electrolyte of 0.2 M CH_3COONa + 0.05 M $Na_2B_4O_7$ for the following pyrocatechol contents: 1) 0; 2) 0.05 mM; 3) 0.10 MM; 4) 0.15 mM 5) 0.2 mM; S = 1/50.

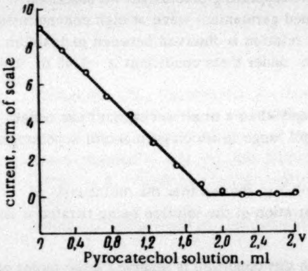


Fig. 2. Titration curve of germanium (6 mM/liter) with 0.1 M pyrocatechol solution in a borate-acetate supporting electrolyte. Initial volume of solution 10 ml; S = 1/50.

Titration of a solution with a germanium content of 5 mM/liter at different pH values showed that on increasing the pH from 6.8 to 9.1 the height of the germanium wave decreases by one third while the amount of pyrocatechol used up in a titration decreases by only 2.6%. Accordingly, at high germanium contents amperometric titration gives more reliable results than the polarographic method.

Pyrocatechol interacts with many elements; accordingly, during determination of germanium in complex materials, germanium must be removed beforehand. This was accomplished by the generally adopted method of extracting with carbon tetrachloride [8].

Germanium can be separated from all elements apart from arsenic by this method. Arsenic in its trivalent form distorts the germanium wave during titration with pyrocatechol. Quinquevalent arsenic, however, does not affect reduction of germanium on the dropping mercury electrode. Accordingly, after extraction of germanium, it is recommended that trivalent arsenic be reduced to its quinquevalent state by means of iodine in the presence of starch.

Germanium is determined as follows. An aliquot of test material (2-4 g for germanium contents up to 1%, 0.2-1 g for germanium contents greater than 1%) is decomposed by the usual method with a mixture of acids, or by fusion with sodium peroxide [9-10]. When the second technique is used, after the melt has been leached it is essential to add hydroxylamine to destroy the hydrogen peroxide.

The test solution, whose volume amounts to 15-30 ml, is transferred to a separating funnel, and concentrated hydrochloric acid in an amount equal to three times the volume of test solution is added, followed by 50 ml of carbon tetrachloride. The mixture to be extracted is then cooled in order to avoid volatilization of germanium, which occurs at elevated temperatures, and extraction is carried out for 2 min. Forty ml of carbon tetrachloride is used for the second extraction; after this extraction the organic layer is washed with 10 ml of 10 N hydrochloric acid.

The germanium is reextracted from the combined extracts with two portions of water, the first of 10 ml and the second of 5 ml. The aqueous solution containing the germanium is transferred to a 25 ml standard flask, the pH is adjusted to eight with the buffer solution (4 M CH_3COONa and 0.1 M $Na_2B_4O_7$), and if necessary with a few drops of 1 N sodium hydroxide, using ZIV-1 or phenolphthalein as indicator. Trivalent arsenic is then oxidized with 0.01 N iodine solution in the presence of two drops of 1% starch solution, and the volume finally made up to the mark with buffer solution.

Ten ml of this solution is transferred to the electrolyzer, and after purging for 5 min with hydrogen, it is titrated at − 1.7 v with 0.1 M pyrocatechol solution delivered from a microburet.

The pyrocatechol solution is standarized amperometrically with a standard germanium solution, using the same supporting electrolyte.

The method which we recommended was checked on samples containing appreciable amounts of copper, zinc, lead, arsenic, and other elements.

Results of amperometric, polarographic, and photometric determinations are compared in Table 2.

This method was also tested on samples to which a standard germanium solution was added.

TABLE 2

Germanium found, %		
Amperometrically	Polarographically	Photometrically
0.25	0.29	–
0.25	0.24	–
0.20	0.22	0.20
0.18	0.21	0.18
0.24	0.24	
0.35	0,34	0.37
2.79	0.79	2.86

TABLE 3

	Germanium			
Amount in test sample, mg	Added,mg	Total taken, mg	Found, mg	Error (relative), %
8.8	7.3	16.1	15.9	1.24
9.5	3.6	13.1	12.7	3.06
1.7	7.3	9.0	8.4	6.67
0.34	7.26	7.6	7.2	5.2

The experimental results are shown in Table 3; it is clear from these results that the mean error is 4.1%.

The method developed can therefore be recommended for the determination of germanium at the level of tenths of a percent and whole percentages.

SUMMARY

A new method has been developed for the amperometric titration of germanium with a pyrocatechol solution; the supporting electrolyte consists of sodium acetate and sodium tetraborate at pH 7-9, while a dropping mercury electrode is used as the indicator electrode.

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AMPEROMETRIC TITRATION OF THORIUM SALTS WITH CUPFERRON

V. D. Vasilenko, E. B. Ostrovskaya and T. S. Fomenko

Dnepropetrovsk State University

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Cupferron has found wide application in chemical analysis for the gravimetric determination of a number of elements. In amperometric titration use is made of the property of cupferron to be reduced on a dropping mercury electrode, and also to be oxidized on a rotating platinum electrode during determination of titanium [1-4], zirconium [5-7], and some rare earths [11]. The composition of the cupferronates of the rare earths of the cerium group which are formed corresponds to the formula $MeCup_3$ [8-11], while that for the cupferronates of the yttrium group of the rare earths corresponds to $MeCup_3$ and NH_4Cup [12].

Thorium also forms sparingly soluble cupferronates; published information on the conditions under which they are formed is, however, contradictory. In all the methods described, it is recommended that the final state in the determination should be calcination to the oxide. Thornton [13] has indicated that it should be possible to precipitate thorium with cupferron from acetic acid solutions not containing free sulfuric acid. Lendell et al [14] recommend that precipitation should be carried out at pH 4 and higher, but also refer to the possibility of precipitating thorium even from very concentrated hydrochloric acid solutions. Eckhert and Bane [15] indicate that thorium forms several complex compounds with cupferron, and that a precipitate is formed on adding cupferron to sulfuric acid solutions of thorium at pH 3.5-4.5.

The aim of the work described here was to establish more accurately the conditions leading to the formation of thorium cupferronate, to determine the composition of the precipitate, to study the effect of foreign ions, and to establish the possibility of titrating thorium amperometrically with cupferron in the presence of the rare earths.

10^{-2} M solutions of chemically pure thorium nitrate, and of the nitrates and chlorides of cerium, lanthanum, praseodymium, neodymium, and yttrium were used in the course of the work. The concentration of the solutions was determined gravimetrically: the oxalate method was used for thorium, and the hydroxyquinoline method for the rare earths.

Cupferron solutions were prepared by the method described by Kul'berg [16] and by Usatenko and Bekleshova [2-3], both with and without the use of a stabilizer—phenacetin. The concentration of the cupferron solutions was determined by amperometric titration of titanium sulfate solutions [2-3]. Citric and sulfosalicylic acids were used as 0.5 M solutions.

The ammonia-acetate buffer solutions were prepared from chemically pure grade reagents. pH was controlled potentiometrically. The remaining reagents were used in the form of their 0.1-0.2 M solutions, while coagulators were used in the form of the chemically pure dry salts.

Titration was carried out with a rotating platinum anode (l = 8 mm, d = 0.5 mm) and a saturated calomel electrode, at an applied potential of 1.0 v. The diffusion current was recorded with a type ϕ galvanometer on a scale with 100 divisions, one whole division being equal to 0.42×10^{-9} amp. Five ml of buffer solution was used when the total volume of solution being titrated was 10-15 ml.

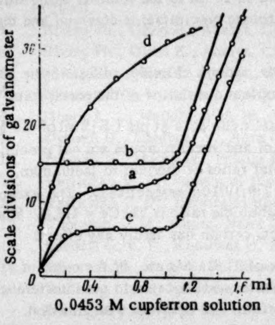
Investigation showed that the most reproducible results for titration of thorium are obtained at ph 3-4. Appreciable formation of a precipitate is observed on addition of approximately 1/4-1/3 of the volume of precipitant corresponding to the equivalence point (fig., a). We originally interpreted this as formation of a complex ion with the composition $ThCup^{3+}$. However, on measuring the value of the diffusion current of solutions containing increasing amounts of equimolar mixtures of thorium nitrate and cupferron, no increase in i_d was observed. Obviously, the first increase in i_d on the titration curve (fig., a) is determined not by formation of a complex ion and its oxidation on the anode, but by the appreciable solubility of the precipitate. The precipitate tends to form a colloid. In order to prevent colloid formation, and to lower the solubility, we tested some electrolyte-coagulators — the chlorides, nitrates,

Table 1 Titration of a Thorium Salt Solution with Cupferron (Total volume 10 ml; pH 4.2; 3 g NaCl).

Thorium M × 10^{-5} taken	M × 10^{-5} cupferron taken for titration	Mean M × 10^{-5} cupferron	M_{Cup}/M_{Th}
0,12	0,47; 0,50; 0,49; 0,50; 0,48;	0,49	4,08
0,24	0,99: 1,00; 0,97; 0,97; 0,88	0,98	4,08
0,48	1,95; 1,90; 1,92; 1,94; 1.93	1,93	4,02
1,20	4,75; 4,70, 4,72; 4,80; 4,73	4,70	3,92
2,80	11,18; 11,12; 11,18; 11,12; 11,15	11,15	3,98
5,60	22,40; 22,60; 22,47; 22,50; 22,54	22,50	4,02

Table 2 Titration of Cupferron Solution with a Thorium Salt (Titration conditions the same as given in Table 1).

M × 10^{-5} cupferron taken	M × 10^{-5} M thorium nitrate solution taken for	Mean	M_{Cup}/M_{Th}
0,50	0,12; 0,13; 0,15; 0,10; 0,15	0,13	3,85
2,00	0,55; 0,45; 0,45; 0,50; 0,45	0,48	4,16
10,00	2,49; 2,52; 2,49; 2,49; 2,50	2,50	4,00
20,00	5,10; 4,96; 4.98: 4.98: 5,08	5,02	3,98



Titration curves of 1.2×10^{-5} M thorium nitrate with 0.0453 M cupferron solution. Volume 10 ml, pH 4.1. a) Without a coagulator; b) with a coagulator, 0.05 mole NaCl; c) in the presence of 0.05 mole $NaNO_3$; d) in the presence of 0.025 mole Na_2SO_4.

and sulfates of the alkali metals and ammonium. In the presence of sulfates, titration of thorium with cupferron is impossible; apparently, the sulfate complex of thorium is more stable than its cupferronate (fig., d). The chlorides proved to be most effective, the best of these being sodium chloride when the amount of it present in 10-15 ml of solution being titrated was 3-5 g (fig., b). Under these conditions a precipitate is formed on adding the first drops of precipitant.

As the results in Tables 1 and 2 show, at the equivalence point the molar ratio of cupferron to thorium is equal to 4:1, both during direct and back titration; this confirms formation of a precipitate with the composition $ThCup_4$. Formation of a precipitate occurs in the course of the first 45-60 sec, accordingly, during titration the current was measured one minute after adding fresh portions of precipitant.

At pH 4 and higher, the rare earths, like thorium, are titrated with cupferron to form precipitates with the composition $MeCup_3$ [11]. As shown below, in the presence of appropriate masking agents, and also on lowering the pH of the solutions below 4, it is possible to carry out selective titration of thorium with cupferron in the presence of the rare earths. The limiting ratio of Th: rare earth for which satisfactory titration results are obtained depends on the pH of the solution and on the nature of the masking agent.

Citric and sulfosalicylic acids, which are used in the analysis of minerals containing thorium and the rare earths, were used as masking agents for the rare earths. Thus the use of citric acid in amounts not greater than 1.0-1.5 ml of 0.5 M solution in buffered solutions with pH 3, when the total volume is 10 ml, makes it possible to determine thorium in the presence of equimolar amounts of the rare earths with reasonable accuracy. However, if the same volume of citric acid is used in solutions not containing buffer mixtures (the pH being equal to 2.0-2.5), then it is possible to determine thorium at molar ratios to the rare earths of 1:2 and even 1:2.5. The relative error does not exceed 3. Increasing the citric acid concentration leads to partial dissolution

Table 3. Determination of Thorium and Total Rare Earths by Amperometric Titration with Cupferron Solution*

Thorium, mg		Mean deviation of an individual determination		Probable deviation of an individual determin.		Rare earths introduced into the mixture, mg	Found in the mixture**	Mean deviation of an individual determination		Probable deviation of an individual determination	
Taken	Found**	Absolute	Relative	Absolute	Relative			Absolute	Relative	Absolute	Relative
0,602	0,606	0,012	2,06	0,011	1,81	1,200	1,244	0,034	2,78	0,031	1,50
0,602	0,606	0,010	1,65	0,008	1,32	2,543	2,600	0,023	0,88	0,020	0,77
0,602	0,615	0,011	1,79	0,010	1,62	2,907	2,948	0,62	2,10	0,050	1,70
2,408	2,394	0,037	1,55	0,030	1,26	4,800	4,906	0,116	2,36	0,096	1,97
6,020	6,035	0,112	1,85	0,098	1,61	25,430	25,969	0,418	1,49	0,320	1,23
6,020	5,816	0,110	1,96	0,090	1,60	29,070	29,408	0,508	1,75	0,432	1,47
8,190	8,364	0,199	2,38	0,174	2,08	16,313	16,216	0,071	0,44	0,041	0,25
8,190	8,368	0,176	2,10	0,167	2,00	39,532	40,243	0,704	1,75	0,564	1,40

*Total Th and rare earths was titrated at pH 4.2 in a volume of 10 - 15 ml.

**Arithmetic mean of 5 determinations.

of the cupferronate, while an increase in the amount of rare earths leads to their coprecipitation with thorium.

Replacement of citric acid by its potassium salt leads to formation of double salts of the rare earths, as shown in [17], and to the formation of thorium precipitates of variable composition, in which the molar ratio of cupferron to thorium increases with increasing concentration of potassium citrate.

The use of sulfosalicylic acid as a masking agent permits readily reproducible titration results to be obtained even at pH 1.7-1.5. Such an increase in acidity does not only increase the solubility of the cupferronates of the rare earths, but also favors increasing adsorption of foreign ions by the thorium cupferronate precipitate. The optimum sulfosalicylic acid content during titration is 0.1-0.15 M (2-3 ml of 0.5 M acid in 10 ml of the solution being titrated). At higher sulfosalicylic acid concentrations dissolution of the thorium cupferronate precipitate is observed and the titration results obtained are low.

Prolonged storage of solutions (30-48 hr) containing thorium cupferronate, sodium chloride, sulfosalicylic acid, and a small excess of cupferron is accompanied by partial and sometimes complete dissolution of the precipitate.

Under the conditions used for titrating thorium, in the presence of sulfosalicylic acid at pH 1.5 (2 ml of 0.5 M HSal*, 3 g NaCl, volume 10 ml), trivalent ions of the rare earths of the cerium and yttrium groups are not precipitated by cupferron. Satisfactory results for thorium are obtained when the molar ratios of thorium to lanthanum, praseodymium, neodymium, and yttrium in mixtures are less than or equal to 1:8:10:10:8 respectively. The exception is trivalent cerium, in the presence of which satisfactory results are obtained when the ratio is Th: Ce = 1:2.5. When, in addition to cerium, other representatives of the rare earths tested are present, cerium has hardly any effect.

Salts of the alkaline earth metals do not interfere with titration at ratios of Th:Ca:Mg etc. of the order of 1:500-800; aluminum and beryllium do not interfere at ratios of 1:400. Phosphates and silicates do not interfere with titration. Trivalent iron, zirconium, and titanium are coprecipitated with thorium, and interfere with titration. Fluorides, sulfates, and sodium ethylenediaminetetracetate interfere with titration.

On the basis of the work carried out, the following method can be recommended for the determination of thorium and total rare earths in mixtures of their salts.

An aliquot of test solution containing from 0.2 to 5-10 mg of thorium and a corresponding amount of the rare earths is transferred to a 50 ml beaker; 3 g of NaCl and 5 ml of buffer solution with pH 5 ± 0.2 are added, and the volume of the solution made up to 10 ml with distilled water (the final pH should be 4-4.5). A rotating platinum electrode is immersed in the solution, as well as the bridge connecting the saturated calomel electrode; a potential of 1 v is applied (with respect to the saturated calomel electrode) and the solution titrated with cupferron solution, the galvanometer readings being taken one minute after each new portion of precipitant is added. Under these conditions, thorium and total rare earths are titrated.

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*Sal represents the anion of sulfosalicylic acid.

To a second aliquot of the same solution is added 3 g NaCl and 2 Ml of 0.5 M sulfosalicylic acid; the volume is made up to 10 ml with water, and the solution titrated. The volume of cupferron solution used up in this case corresponds to the thorium content.

For thorium contents of less than 2.0 mg it is recommended that titration be carried out with 0.01-0.02 M cupferron solution, while for thorium contents of 1-10 mg, titration is carried out with 0.05 M cupferron solution; at higher thorium concentrations, in the presence of large amounts of the rare earths, it is recommended that 0.07-0.1 M cupferron solutions be used for titrating.

Results for the determination of thorium and total rare earths given in Table 3 show that reasonably good reproducibility and accuracy are possible.

SUMMARY

Thorium forms a precipitate of composition $ThCup_4$ with cupferron over a wide pH range in the absence of strong acids and sulfates. The precipitate tends to form a colloid, and coagulators must be used; sodium chloride is the most efficient for this purpose.

Sulfosalicylic acid exhibits a stronger masking effect than citric acid during titration of thorium in the presence of the rare earths.

Optimum conditions have been established for the amperometric titration of thorium in the presence of cerium group rare earths. The method suggested has been checked on synthetic mixtures. The reproducibility and accuracy of the method are satisfactory.

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ANODE AMPEROMETRIC TITRATION OF BISMUTH ON THE BASIS OF THE FORMATION OF IODOBISMUTHITES

A. K. Zhdanov and T. A. Desyatova

V. I. Lenin Tashkent State University

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We have shown previously that it is possible to carry out quantitative amperometric determination of bismuth on the basis of the formation of the iodobismuthites of 8-hydroxyquinoline [1] and pyramidone [2], and that amperometric titration can be carried out on the basis of both the cathode and anode current. In the first instance [1], bismuth is titrated with a dropping mercury electrode and with rotating platinum microelectrodes, while in the second instance bismuth can only be titrated with a dropping mercury electrode. On the basis of the fact that certain other organic bases are also capable of forming sparingly soluble compounds with potassium iodobismuthite [3-6] in acid media, we decided to investigate the possibility of using some of these bases for the quantitative determination of bismuth by an anode amperometric method on a setup provided with a rotating platinum microelectrode.

Experiments on amperometric titration of bismuth with potassium iodide in the presence of organic bases were carried out as before [1], on the basis of the oxidation current of iodide ions at a platinum electrode potential of +0.44 v, and using a setup of the usual type provided with a rotating platinum microelectrode. At higher potentials the platinum electrode becomes covered with a black precipitate of iodine. By titrating on the basis of the anode current, interference from oxygen and a number of other readily reduced ions is avoided. A saturated calomel half-element with a large mercury surface was used as the nonpolarizing electrode. The electrolyte bridge which connected the solution being titrated with the calomel half-element through an intermediate vessel containing potassium chloride was filled with potassium nitrate solution. The current was measured with a mirror galvanometer fitted with a shunt. The platinum electrode, which was rotated at 700 rpm, was a glass tube 10 mm in diameter with a fused side arm close to the lower sealed end with a platinum wire 0.4 mm in diameter and 4 mm long. Titration was carried out in the usual 100 ml beakers. The potassium iodide solution was added from a tapless microburet of the Shilov type; the capacity of the buret was 5 ml, while the scale divisions were 0.02 ml. The platinum electrode was cleaned with concentrated nitric acid and rinsed with water before each titration.

Table 1. Titration of Bismuth with Potassium Iodide in the Presence of 500 mg Antipyrine in a Supporting Electrolyte of 2.5 M Sulfuric Acid. Titration on the Basis of the Anode Current (mean of 4-5 determinations)

Bismuth, mg		Deviation of the mean found from that taken, %
Taken	Found	
43,80	43,58	0,52
32,85	32,68	0,51
20,98	20,99	0,04
10,49	10,62	1,15
5,25	5,83	11,04

The potassium iodide solution was prepared by dissolving an accurately weighed amount of the chemically pure salt in water, while the bismuth nitrate solution was prepared by dissolving an aliquot of chemically pure bismuth metal in nitric acid (1:1), followed by dilution to a definite volume with water. The amount of nitric acid taken was sufficient to dissolve the bismuth and to give a final solution with an acidity of 0.4 N.

Titration was carried out as follows. 0.5 g of the organic base was added to the bismuth nitrate solution contained in a beaker. The optimum acidity of the solution for carrying out titration of bismuth had been determined beforehand in special experiments; the requisite acidity was then obtained by adding a known amount of 18 N sulfuric acid and water. The volume of solution being titrated was 40 ml in all experiments. The requisite potential of the indicator electrode was applied and titration with potassium iodide carried out. The initial value of the current was recorded, and subsequently the current was recorded after addition of each portion of reagent; initially the reagent was added in large aliquots to the appearance of a large current, but toward the end the reagent was added in small amounts, 1-2 drops. The end point was established by the usual graphical method.

Table 2. Titration of 21.22 mg of Bismuth with Potassium Iodide in the Presence of Foreign Ions in a Supporting Electrolyte of 2.5 M Sulfuric Acid, at a Platinum Electrode Potential of +0.44 v, and in the Presence of Antipyrine (mean of 4-5 determinations)

Foreign salt	Molar ratio	Bismuth found, mg	Dev. of the mean found from that taken, %	Foreign salt	Molar ratio	Bismuth found, mg	Dev. of the mean found from that taken %
KNO_3	100	20,95	1,27	$Pb(NO_3)_2$	1	21,14	0,38
KNO_3	50	21.21	0,05	$FeSO_4$	100	21,14	0,38
$KC_2H_3O_2$	200	21,16	0,27	$MnSO_4$	100	21,30	0,38
KCl	20	20,46	3,59	$CoSO_4$	50	21,10	0,55
KCl	10	21,10	0,55	$ZnSO_4$	50	21,18	0,18
KCl	5	21,22	0,00	$KAl(SO_4)_2$	100	21,26	0,18
(EDTA-Na)	100	21,06	0,73	$NiSO_4$	50	21,34	0,55
(EDTA-Na)	50	21,10	0,60	$MgSO_4$	100	21,33	0,50
Tartaric acid	200	21,37	0,69	$Cr_2(SO_4)_3$	50	21,33	0,50
Tartaric acid	100	21,26	0,19	$CdSO_4$	5	21,67	2.12
Na_2HPO_4	100	21,19	0,14	$CdSO_4$	2,5	21,14	0,38
Citric acid	50	21,38	0,75	Antimonyl potassium tartrate	1	21,26	0,18
Citric acid	100	21,42	0,93				
$Pb(NO_3)_2$	25	20,05	5,57	Sodium arsenite	1	20,99	1,08

Titration of Bismuth with Potassium Iodide in the Presence of Antipyrine. During titration of equal amounts of bismuth (20.98 mg in 40 ml of solution) with potassium iodide in the presence of 500 mg antipyrine at a platinum electrode potential of +0.44 v, it was established that satisfactory results, close to the true values, are obtained when the acidity of the solution being titrated is 2.5 M. At lower acidities high results are obtained for bismuth, while at very high acidities the results are low, the results being lower the higher the acidity of the solution being titrated. Thus in the presence of antipyrine, as before in the presence of pyramidone [2], the optimum acidity of the solution being titrated is 2.5 M. The amount of antipyrine used during titration of bismuth with potassium iodide should be 20-40 times that of the bismuth.

As Table 1 shows, the results of titrating bismuth are completely satisfactory and are reasonably reproducible. There is a fairly good proportionality between the amount of potassium iodide used and the amount of bismuth: four iodide ions correspond to one bismuth ion.

It is clear from Table 2 that even very large amounts(100-200×)of nitrates, acetates, tartrates, citrates, sulfates, and phosphates, as well as sodium ethylenediaminetetracetate do not interfere with bismuth titration. Chloride ions at concentrations not greater than ten times that of bismuth do not interfere with titration of the latter. At higher concentrations chloride ions lower the results for the titration of bismuth, since, apparently, they partly enter into the composition of the bismuth complex instead of the iodide ions.

Many cations do not interfere either. Thus even very large (50-100 ×) amounts of divalent iron, manganese, zinc, aluminum, magnesium, cobalt, nickel, and chromium do not interfere during bismuth titration. Appreciable amounts of lead, cadmium, trivalent antimony, and arsenic interfere. Satisfactory results can be obtained for bismuth when the amount of lead, trivalent antimony, and arsenic is the same as that of bismuth (1:1). When cadmium is present, bismuth can only be titrated when the cadmium concentration is not more than three times that of bismuth.

The method developed has been checked on synthetic mixtures of chemically pure metals (58.14%, Bi, 16.62% Cd, and 25.24% Pb). 2.0849 g of alloy was dissolved in 20 ml nitric acid (1:1), the solution was transferred to a 500 ml standard flask and its volume made up to the mark with water. An aliquot of this solution was titrated by the anode amperometric method with potassium iodide in the presence of antipyrine. The mean of five determinations of bismuth in the mixture deviated by 0.20% from the amount taken.

Titration of Bismuth with Potassium Iodide in the Presence of Pyramidone. It has been shown earlier that it is possible to titrate bismuth amperometrically with potassium iodide in the presence of pyramidone on a setup with a dropping mercury electrode [2]. Taking into account the advantages of a rotating solid microelectrode over a dropping mercury electrode, in the course of the work described here we studied the possibility of determining bismuth by an anode amperometric method using a rotating platinum microelectrode in the presence of pyramidone.

Table 3. Anode Titration of Bismuth with Potassium Iodide in the Presence of 500 mg Pyramidone in a Supporting Electrolyte of 2.5 M Sulfuric Acid (mean of 4-5 parallel determinations)

Bismuth, mg		Deviation of the mean value found from that taken%
Taken	Found	
43,80	43,97	0,39
32,85	32,66	0,57
31,47	31,53	0,19
20,98	20,90	0,38
10,95	10,62	3,01
5,25	5,60	6,66

Table 4. Anode Titration of Bismuth with Potassium Iodide in the Presence of 200 mg β - Naphthoquinone in a Supporting Electrolyte of 3.5 M Sulfuric Acid (mean of 5-6 parallel determinations)

Bismuth, mg		Deviation of the mean value found from that taken %
Taken	Found	
54,50	54,53	0,05
43,60	43,58	0,04
41,32	41,62	0,73
32,70	32,70	0,00
20,66	20,72	0,29
16,35	16,30	0,31
10,33	10,68	3,38

Experiments on the amperometric titration of equal amounts (20.98 mg in 40 ml) of bismuth with potassium iodide in the presence of pyramidone, at various acidities of the solution being titrated, showed that the best results are obtained at an acidity of 2.5 M, as during titration with a dropping mercury electrode. At lower acidities the results are high, while at higher acidities they are low.

It is clear from Table 3 that anode amperometric titration of bismuth in the presence of pyramidone gives fairly accurate and reproducible results during determination of various amounts of bismuth. Solutions containing small amounts of bismuth are not titrated so well because of the solubility of the precipitate.

We did not study the influence of foreign ions on the results of titrating bismuth in the presence of pyramidone in the work described here, since it has been studied earlier during titration of bismuth with a dropping mercury electrode [2]. Those anions and cations which do not interfere during titration in the presence of antipyrine and 8-hydroxyquinoline, should not interfere with titration of bismuth with potassium iodide (in the presence of pyramidone) by the anode amperometric method.

Titration of Bismuth with Potassium Iodide in the Presence of β-Naphthoquinoline. On the basis of the capacity of β-naphthoquinoline to precipitate bismuth from acid solutions in the presence of chloride, bromide, iodide, and thiocyanate ions, we thought it would be interesting to investigate the possibility of using it for determining bismuth by anode amperometric titration with potassium iodide.

Experiments on the titration of equal amounts of bismuth (20.66 mg) in 40 ml of solution showed that again in this case the results depend on the acidity of the solution being titrated. The best results, i.e. those nearest the true values, are obtained on titrating in a supporting electrolyte of 3.5 M sulfuric acid (Table 4). At lower acidities the results are high, while at higher acidities they are low. The amount of β-naphthoquinoline should not exceed the amount of bismuth in the solution being titrated by more than 30-40 times. In our experiments the amount varied from 75 to 300 mg. The presence of large amounts of β-naphthoquinoline leads to a slight increase in the results.

Presumably those anions and cations which do not interfere during titration in the presence of antipyrine, pyramidone, and 8-hydroxyquinoline, should not interfere during titration of bismuth by the given method in the presence of 8-naphthoquinoline.

Titration of Bismuth with Potassium Iodide in the Presence of Some Other Organic Bases (Cinchonine, Quinine, and Anabasine). Finally we established, in principle, the possibility of using cinchonine, quinine, and anabasine for the amperometric titration of bismuth with potassium iodide. During titration of strongly acid solutions of bismuth containing an excess of any one of the organic bases mentioned, the limiting current is established fairly rapidly after addition of each portion of reagent, while the titration curves obtained are very clearly defined and have an almost horizontal left hand branch and a sharply rising right hand branch. The precipitates of cinchonine and quinine iodobismuthites formed during titration are reminiscent in character and color of the precipitates obtained in the presence of 8-hydroxyquinoline, pyramidone, antipyrine, and β-naphthoquinoline (reddish-orange color). In the presence of anabasine the precipitates obtained are a red Bordeaux color. There is a fairly good linear relation between the amount of bismuth taken and the volume of potassium iodide used in the titration.

During titration of bismuth in the presence of cinchonine and quinine, the acidity should be about 6 M with respect to sulfuric acid, while for anabasine it should be about 3 M. For titration in the presence of 8-hydroxyquinoline, pyramidone, and antipyrine the optimum acidity is 2.5 M, while in the presence of β-naphthoquinoline it is 3.5 M. 150-200 mg of the corresponding base is used in each titration.

SUMMARY

The possibility has been established and conditions have been found for the direct amperometric titration of bismuth with potassium iodide in the presence of antipyrine, with a rotating platinum microelectrode. Nitrates, sulfates, phosphates, acetates, tartrates, and citrates, as well ad EDTA-Na, do not interfere with the titration when present in amounts which are 100-200 times that of the bismuth. Chloride ions do not interfere as long as their concentration is not higher than ten times that of the bismuth. Aluminum, zinc, magnesium, cobalt, nickel chromium, manganese, and iron even in amounts which are 50-100 times that of bismuth do not interfere. Small amounts of lead (1:1), trivalent antimony (1:1), arsenic (1:1), and cadmium (3:1) do not interfere either.

The possibility has been demonstrated and conditions have been established for titrating bismuth in the presence of pyramidone or β-naphthoquinoline, and also in the presence of cinchonine, quinine, and anabasine by an anode amperometric method.

The amperometric method of determining bismuth in the presence of antipyrine has been checked on an alloy containing bismuth, cadmium, and lead.

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A STUDY OF THE INTERACTION OF QUINQUEVALENT MOLYBDENUM WITH ETHYLENEDIAMINETETRACETIC ACID

A. E. Klygin, N. S. Kolyada, and D. M. Zavrazhnova

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Quinquevalent molybdenum exists in solutions with hydrochloric acid concentrations of less than 2 M in the form of yellow-brown ions [1]. At pH values higher than 3.0 the sparingly soluble hydroxide MoO_2OH is formed. During the interaction of MoO_2^+ ions with sodium ethylenediaminetetracetate (EDTA-Na, Complexon III) a yellow colored compound is formed. The stoichiometric cofficients in the equation of the reaction, as determined by the Ostromyslenskii-Job method [2], and by preparative [2], and titrimetric methods [3,4] have shown that two MoO_2^+ ions interact with one mole of ethylediaminetetracetate. The product isolated from aqueous-ethanol solutions at pH 6.0 has a composition which corresponds to the formula

$$Na_2[MoO_2(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2MoO_2]H_2O$$

Aqueous solutions of the compound are stable over a wide acidity range: from 0.5 M HCl to pH 10.0 [3]. The formation constant of the ethylenediaminetetracetate of quinquevalent molybdenum is unknown. There are no available metallo-indicators for quinquevalent molybdenum; accordingly, the latter is titrated complexometrically by titrating excess EDTA-Na with solutions of various salts, using appropriate metallo-indicators. Titration with zinc sulfate at pH 10 in the presence of eriochrome black T is a complexometric method with low selectivity [3]. The selectivity of the method can be increased by titrating with cupric sulfate, using the indicator pyridylazonaphthol at pH 4.0 [4]. It is well known that the yield of ethylenediaminetetracetates of various metals is determined by their formation constants and by the pH of the solution. If quinquevalent molybdenum could be complexed with EDTA-Na, and then excess of the latter titrated with a solution of a salt of a metal which forms a sufficiently stable compound with EDTA-Na, such a titration could be carried out in fairly acid solutions, and this in turn would ensure a method with relatively high selectivity for determining quinquevalent molybdenum.

We have determined the formation constant of the ethylenediaminetetracetate of quinquevalent molybdenum and have developed a more selective complexometric method for the determination of the latter.

Requisite Reagents. 1. Ammonium Molybdate, 1.16×10^{-2} M. 2.05 g of ammonium heptamolybdate was dissolved in one liter of distilled water. The concentration was established gravimetrically by the 8-hydroxyquinoline method [5]. 2. EDTA-Na, 2.384×10^{-2}M solution. The molarity was established against a standard solution of thorium nitrate [6]. 3 Hydrazine Sulfate – 0.5% aqueous solution. 4. Zirconyl Sulfate 1.979×10^{-2}M solution. 6.5 g of zirconyl sulfate was dissolved in one liter of 1 N sulfuric acid. The concentration of the solution was established by precipitating zirconyl hydroxide with ammonia, calcining the precipitate, and weighing it as ZrO_2. 5. Xylenol Orange – 0 05% aqueous solution.

Spectrophotometric Study of the Interaction of MoO_2^+ Ions with Ethylenediaminetetracetic Acid. Hydrazine sulfate in a solution which is 1 N with respect to sulfuric acid [3,4], on boiling for 3-5 min, ensures quantitative reduction of sexivalent molybdenum to the quinquevalent state. At room temperature the optical density of the yellow-brown colored solutions obtained remains constant for 10-15 min, and then gradually decreases. On adding EDTA-Na to the yellow-brown sulfuric acid solution of the quinquevalent molybdenum compound heated to the boil, the color changes to yellow. When stoichiometric concentrations of the reactants are used, the optical density of such solutions, after cooling to room temperature, increases with time and reaches a constant value 15 min after the solutions have been prepared.

The molar extinction coefficient of solutions of the compound of quinquevalent molybdenum with ethylenediaminetetracetic acid (ϵ_t) was determined by the saturation method. This was carried out as follows: to various volumes of 1.16×10^{-2}M ammonium molybdate solution was added 25 ml of 1 N sulfuric acid and the solutions heated to the boil; 10 ml of 0.5% hydrazine sulfate solution was then added to each solution and the solutions again boiled for 5 min. Twenty ml of 2.38×10^{-2}M EDTA-Na was added to each solution and the latter again brought to the boil.

Table 1. Molar Extinction Coefficient of Solutions of Quinquevalent Molybdenum Complexonate at 387 mμ

Initial molybdenum concentration (C_i), M	Optical density (D_i)	ϵ_t	Initial molybdenum concentration (C_i), M	Optical density (D_i)	ϵ_t
$1,16 \cdot 10^{-4}$	0,066	379	$6,96 \cdot 10^{-4}$	0,370	354
$2,32 \cdot 10^{-4}$	0,133	382	$8,12 \cdot 10^{-4}$	0,433	356
$3,48 \cdot 10^{-4}$	0,189	362	$9,28 \cdot 10^{-4}$	0,520	373
$4,64 \cdot 10^{-4}$	0,250	359	$1,04 \cdot 10^{-3}$	0,550	351
$5,80 \cdot 10^{-4}$	0,313	360	$1,16 \cdot 10^{-3}$	0,620	356

The solutions obtained were cooled to 20°, transferred to 100 ml standard flasks, diluted with water to the mark, and mixed. The optical density (D_i) of these solutions, like that of all subsequent solutions, was measured on a SF-4 quartz spectrophotometer at 387 mμ relative to distilled water. Our results confirmed published information [3] that the maximum light absorption of the compound of quinquevalent molybdenum with EDTA-Na lies in this region; quinquevalent molybdenum ions in sulfuric acid solution, as in hydrochloric acid solution [3], exhibit a relatively low absorption (see Table 2), while EDTA-Na hardly absorbs at all. ϵ_t was calculated by means of the equation where

$$\varepsilon_t = \frac{D_i}{\frac{C_i}{2}\, l},$$

C_i is the initial molybdenum concentration, M/L; l is the path length, equal to 3 cm.

Table 2. Formation Constant of the Ethylenediaminetetracetate of Quinquevalent Molybdenum at 20°
(initial molybdenum concentration $C_1 = 1.16 \times 10^{-3}$ M; initial EDTA-Na concentration 7.158×10^{-4} M. The ionic strength was varied between 0.3 and 0.7 by means of the reagents)

Initial H_2SO_4 concentration, M	Optical density of the solutions		Equilibrium concentrations of the reactants				
	Mo^V, $D_{MoO_2^+}$	Mo^V in the presence of EDTA-Na D	$[H^+]$	t	$[MoO_2^+]$	$[H_2Y^{2-}]$	$K \cdot 10^{-11}$
0,143	0,054	0,165	0,153	$4,12 \cdot 10^{-4}$	$3,36 \cdot 10^{-4}$	$4,64 - 10^{-8}$	0,79
0,201	0,053	0,162	0,212	$4,04 \cdot 10^{-4}$	$3,52 \cdot 10^{-4}$	$1,56 \cdot 10^{-8}$	2,09
0,260	0,052	0,147	0,271	$3,52 \cdot 10^{-4}$	$4,56 \cdot 10^{-4}$	$7,48 . 10^{-9}$	2,26
0,378	0,055	0,116	0,389	$2,26 \cdot 10^{-4}$	$7,08 \cdot 10^{-4}$	$2,57 \cdot 10^{-9}$	1,75
0,437	0,054	0.107	0,448	$1,97 \cdot 10^{-4}$	$7,66 \cdot 10^{-4}$	$1,57 \cdot 10^{-9}$	2,14
0,496	0,055	0,097	0,507	$1,56 \cdot 10^{-4}$	$8,48 \cdot 10^{-4}$	$1,05 \cdot 10^{-9}$	2,07
0,584	0,056	0,076	0,595	$7,42 \cdot 10^{-5}$	$1,01 \cdot 10^{-3}$	$6,41 \cdot 10^{-10}$	1,14

It follows from the results given in Table 1 that despite varying the amount of excess EDTA-Na from 80 to 8 times that stoichiometrically necessary, the molar extinction coefficient remains almost constant (within the limits of experimental error). Accordingly, under the conditions indicated, all the quinquevalent molybdenum is found in the form of a compound with ethylenediaminetetracetic acid. The mean value of the molar extinction coefficient $\epsilon_t = 363 \pm 8$ at a confidence level of 0.95 [7].

The complex formation constant was determined as follows. Ten ml portions of 1.16×10^{-2}M ammonium molybdate solution were introduced into a series of beakers, and the sexivalent molybdenum reduced with hydrazine sulfate as indicated above. Three ml portions of 2.386×10^{-2}M EDTA-Na solution was then added to each, the solutions were brought to the boil and then cooled to 20°. The solutions were next transferred to 100 ml standard flasks containing varying amounts of sulfuric acid, the volumes made up to the mark with water, and the solutions mixed.

In order to determine the molar extinction coefficients of quinquevalent molybdenum in sulfuric acid solutions under the same conditions, experiments were carried out with solutions containing all the components apart from EDTA-Na. Three solutions were prepared at the same time and the optical density measured 15 min after pouring the solutions together in a cell with a path length of 1 cm. The results are given in Table 2.

Sulfuric acid is a strong acid in its first dissociation stage and relatively weak in its second ($K_2 = 1.2 \times 10^{-2}$). Column 4, Table 2 contains the values of the hydrogen ion concentration obtained by adding the molar concentration of sulfuric acid and the hydrogen ion concentration calculated on the basis of the second dissociation constant.

From the results given in column 2 (constancy of optical density) it follows that on changing the sulfuric concentration from 0.143 to 0.584 M, the quinquevalent molybdenum ions are not subjected to any changes. As a result of calculation, and of a statistical treatment of the results obtained [7], it was found that the molar extinction coefficients of quinquevalent molybdenum ions at 387 mμ $\epsilon_{MoO_2^+} = 46.7 \pm 1.1$ at a confidence level of 0.95.

In accordance with published results [2-4], complex formation in the test system proceeds according to the scheme

$$2MoO_2^+ + H_{4-n}Y^{n-} = (MoO_2)_2 H_{4-n}Y^{(n-2)-}, \quad K = \frac{[(MoO_2)_2 H_{4-n}Y^{(n-2)-}]}{[MoO_2^+]^2 [H_{4-n}Y^{n-}]}. \tag{1}$$

Let us assume that the initial concentration of MoO_2^+ ions is C_1 M while that of EDTA-Na is C_2 M, and the equilibrium concentration of the complex compound is

$$[(MoO_2)_2 H_{4-n}Y^{(n-2)-}] = tM$$

Then the equilibrium concentration of $[MoO_2^+]$ will be equal to

$$[MoO_2^+] = C_1 - 2_t \tag{2}$$

At 387 mμ only the complex compound and MoO_2^+ absorb, accordingly, the optical density of the solution, measured experimentally – (D), is equal to the sum of the optical densities of the MoO_2^+ ions ($D_{MoO_2^+}$) and of the complex compound (D_t)

$$D = D_{MoO_2^+} + D_t \tag{3}$$

Substituting the values of the optical densities from the expression for Beer's law in equation (3) and solving the equation obtained with respect to t, we find:

$$t = \frac{D - \varepsilon_{MoO_2^+} l C_1}{l\left(\varepsilon_t - 2\varepsilon_{MoO_2^+}\right)} \tag{4}$$

Results of calculations of t by means of equation (4) and of $[MoO_2^+]$ by means of equation (2) are given in columns 5 and 6 of Table 2.

Over the hydrogen ion concentration range which we tested, ethylenediaminetetracetic acid (H_4Y) adds on an additional two hydrogen ions to its amino groups [8], and is converted into H_6Y^{2+}. Accordingly, for calculating the equilibrium concentrations of the various forms of the dissociation of ethylenediaminetetracetic acid, it is necessary to take into account the following processes and the equilibriums corresponding to them:

$$H_6Y^{2+} = 2H^+ + H_4Y \quad K_0[H_6Y^{2+}] = [H^+]^2[H_4Y]. \tag{5}$$

$$H_4Y = H^+ + H_3Y^- \quad K_1[H_4Y] = [H^+][H_3Y^-] \tag{6}$$

$$H_3Y^- = H^+ + H_2Y^{2-} \quad K_2[H_3Y^-] = [H^+][H_2Y^{2-}] \tag{7}$$

$$H_2Y^{2-} = H^+ + HY^{3-} \quad K_3[H_2Y^{2-}] = [H^+][HY^{3-}] \tag{8}$$

$$HY^{3-} = H^+ + Y^{4-} \quad K_4[HY^{3-}] = [H^+][Y^{4-}], \tag{9}$$

where $K_0 = 1.24 \cdot 10^{-2}$ [8], $K_1 = 6.13 \cdot 10^{-3}$ [8], $K_2 = 1.71 \cdot 10^{-3}$ [8], $K_3 = 6.92 \cdot 10^{-7}$, $K_4 = 5.47 \cdot 10^{-11}$ [9].

In addition, taking into account all the transformations of H_6Y^{2+} one can write

$$(C_2 - t) = [H_6Y^{2+}] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]. \tag{10}$$

By solving equations (5-10) simultaneously with respect, e.g., to $[H_2Y^{2-}]$, $[Y^{4-}]$ respectively, we obtain:

$$[H_2Y^{2-}] = \frac{(C_2 - t)\, K_0K_1K_2\, [H^+]^2}{[H^+]^6 + K_0[H^+]^4 + K_0K_1[H^+]^3 + K_0K_1K_2[H^+]^2 + K_0K_1K_2K_3[H^+] + K_0K_1K_2K_3K_4} \tag{11}$$

$$[Y^{4-}] = \frac{(C_2 - t)\, K_0K_1K_2K_3K_4}{[H^+]^6 + K_0[H^+]^4 + K_0K_1[H^+]^3 + K_0K_1K_2[H^+]^2 + K_0K_1K_2K_3[H^+] + K_0K_1K_2K_3K_4} \tag{12}$$

A comparison of equations (11) and (12) shows clearly $\left(\frac{[H_2Y^{2-}]}{[Y^{4-}]} = \frac{[H^+]^2}{K_3K_4}\right)$, that the hydrogen ion concentration has a decisive effect on the yield of the different forms of ethyelendiaminetetracetic acid. Accordingly, the values of the formation constant $(MoO_2)_2H_{4-n}Y^{(n-2)}$, calculated at different hydrogen ion concentrations, will only be constant when the equilibrium concentration of the anion actually participating in the reaction leading to the formation of the compound [10] is substituted in equation (1). For all the other anions not reacting with MoO_2^+ ions, the values of the constants will have a systematic character which is a function of the hydrogen ion concentration. Calculations showed that only the H_2Y^{2-} anions which react with MoO_2^+ according to the equation enter into the reaction.

$$2\,MoO_{+2} + H_2Y^{2-} = (MoO_2)_2H_2Y,\ K = \frac{[(MoO_2)_2H_2Y]}{[MoO_2^+]^2[H_2Y^{-2}]} \tag{13}$$

H_3Y^-, HY^{3-}, and Y^{4-} anions do not participate in the reaction. Thus the values of the formation constant of the compound $(MoO_2)_2Y^{2-}$ vary from 5.2×10^{25} to 1.1×10^{27} on changing the hydrogen ion concentration from 0.155 to 0.596 M. Results of calculations of the concentration of H_2Y^{2-} by means of equation (11) are given in column 7, Table 2. Values of the formation constant calculated by means of equation (13) are given in column 8. The constancy of the values of the constant serves as proof of the fact that the stoichiometric coefficients in the equation of the reaction, the composition of the ions from which the compound $(MoO_2)_2H_2Y$ is formed, and also the molar extinction coefficients of the MoO_2^+ ion and the compound $(MoO_2)_2H_2Y$ [10] have all been determined correctly. The mean value of the formation constant of $(MoO_2)_2H_2Y$ is equal to $K = (1.75 \pm 0.52) \times 10^{11}$ at a confidence level of 0.95.

Table 3. Yield of MoO_2H_2Y as a function of pH at $C_1 = 2 \times 10^{-3}$ and $C_2 = 1 \times 10^{-3}$M.

pH	Yield of $(M_0O_2)_2H_2Y$, %	pH	Yield of $(M_0O_2)_2H_2Y$, %
0,31	10,0	4,5	98,9
1,00	87,0	5,0	98,9
2,0	97,2	8,0	95,4
		10,0	77,2

We calculated the yield of $(MoO_2)_2HY_2$ (Table 3) from the values of the complex formation constant by means of equations (11) and (13).

From the results given in Table 3, and also taking into account the fact that equilibrium is established slowly in the system, it can be concluded that direct complexometric titration of quinquevalent molybdenum at 20° and with an accuracy of down to 0.1% is impossible. Nevertheless, by adding a sufficient excess of EDTA-Na, molybdenum can be quantitatively complexed as a complex compound which is suitable for spectrophotometric determination [11].

Complexometric Determination of Quinquevalent Molybdenum By Titration of Excess EDTA-Na with Standard Zirconium Sulfate Solution. In accordance with the investigations outlined above, and on the basis of published data [3,4], molybdenum can be determined complexometrically in solutions heated to 70-100°, and then only by titrating excess EDTA-Na with a suitable indicator. We decided to titrate excess EDTA-Na with zirconium sulfate solution, using xylenol orange as indicator [6].

Table 4. Results of a Statistical Treatment of Experimental Data on the Determination of Molybdenum in Solutions of its Salts and in the Presence of Impurities

Added, mg		No. of molybdenum determinations, n	Molybdenum found (mean of n determinations), mg	Mean square error	
Molybdenum	Impurity			mg	% (relative)
1,98	—	11	1,99	$\pm 6,4 \cdot 10^{-2}$	±3,2
9,91	—	11	9,98	$\pm 6,1 \cdot 10^{-2}$	±0,6
19,82	—	11	19,97	$\pm 5,9 \cdot 10^{-2}$	±0,29
1,98	100—UO_2^{2+}	11	1,99	$\pm 8,0 \cdot 10^{-2}$	±4,02
9,91	100—UO_2^{2+}	11	9.93	$\pm 5,9 \cdot 10^{-2}$	±0,59
11,13	10—Th^{4+}	11	11,13	$\pm 5,9 \cdot 10^{-2}$	±0,53
11,13	25—Al^{3+}	11	11,18	$\pm 5,2 \cdot 10^{-2}$	±0,46
11,13	1000—$NaNO_3$	8	11,18	$\pm 8,5 \cdot 10^{-2}$	±0,76

Preliminary experiments showed that the most clearly defined indicator color change from yellow to red is observed on titrating EDTA-Na solution prepared in a solution of 0.25 N sulfuric acid and 4×10^{-2}M sodium sulfate, and heated to the boil beforehand, with a solution of zirconium sulfate (1 N with respect to sulfuric acid). As a result of titrating 10 ml of 1.85×10^{-2}M EDTA-Na solution with 1.979×10^{-2} M zirconium sulfate solution under the conditions indicated above the following values for the normality of the EDTA-Na were obtained:

$1,880 \cdot 10^{-2}$
$1,882 \cdot 10^{-2}$
$1,880 \cdot 10^{-2}$
$1,876 \cdot 10^{-2}$
$1,880 \cdot 10^{-2}$
$1,884 \cdot 10^{-2}$
$1,880 \cdot 10^{-2}$
$1,880 \cdot 10^{-2}$
$1,880 \cdot 10^{-2}$
$1,874 \cdot 10^{-2}$
$1,884 \cdot 10^{-2}$

The mean square error of a single determination [7] is ± 3×10^{-5}M or ± 0.17% (relative). Accordingly, this method was used for the determination of the concentration of EDTA-Na in pure solutions, and also, as will be shown below, in the presence of most metal ions apart from trivalent iron, bismuth, and MoO_2^+, which form complex compounds with EDTA-Na in acid solutions. It was established that the titration conditions indicated can be used for determining molybdenum, by complexing it beforehand with excess EDTA-Na into the compound $(MoO_2)_2H_2Y$, and titrating excess of the EDTA-Na with zirconium sulfate. In order to check the method of determining molybdenum in solutions of its salts and in the presence of impurities, the amounts of molybdenum indicated in Table 4, in the form of an aqueous ammonium molybdate solution, were introduced into a series of 250 ml conical flasks; various amounts of the impurites were then added, followed by 25 ml of 1 N sulfuric acid. In experiments with $NaNo_3$ 4-5 g of urea was added in addition, in order to prevent oxidation of the quinquevalent molybdenum.

Table 5. Results of a Statistical Treatment of Experimental Data on the Determination of Molybdenum in Alloys with Uranium

Molybdenum content of the alloy, %	No. of determinations	Molybdenum found %	Mean square error	
			% (absolute)	% (relative)
3.60	12	3.61	$\pm 6.6 \cdot 10^{-2}$	±1.8
4.50	11	4.47	$\pm 4.2 \cdot 10^{-2}$	±0.9
8.96	8	8.96	$\pm 7.9 \cdot 10^{-2}$	±0.9

The solutions obtained were heated to the boil, and 15 ml of a 0.5% solution of hydrazine sulfate prepared in 1 N sulfuric acid added. During the boiling stage, as a result of reduction of molybdenum, the solutions acquired a brownish-yellow color. Three grams of sodium sulfate was next added to each solution, and the latter boiled for another 2-3 min. Standard EDTA-Na solution 2.384×10^{-2}M was added to the hot solutions, the amount added being sufficient to complex the quinquevalent molybdenum stoichiometrically into the compound $(MoO_2)_2H_2Y$, plus an additional 5–7 ml in excess; at this stage the color of the solution changed to a definite yellow. Hot distilled water was added immediately in such an amount as to give a final solution with a concentration of 0.25 N with respect to sulfuric acid (the volumes of all the reagents taken for analysis being taken into account), the solution was again heated to the boil and 1 ml of xylenol orange solution added [6]. Excess EDTA-Na was titrated with the zirconium sulfate solution in sulfuric acid, with constant stirring until the yellow color changed to a distinct red which did not change for 30 sec. In the presence of Al^{3+} ions, after addition of the xylenol orange, a red color appeared, but during titration this color disappeared and did not interfere with the determination of the titration end point. Results of these determinations are given in Table 4.

The results given in Table 4 allow one to conclude that metal ions which form compounds having pk≥ 16 with EDTA-Na (Al^{3}+, Mg^{2}+, Zn^{2}+, Cd^{2}+, Mn^{2} + Co^{2}+, Pb^{2}+, La^{3}+ − Nd^{3}+) should not interfere with molybdenum determination when they are present in the solution to be titrated in amounts of about one millimole.

The method has been checked on alloys of uranium with molybdenum. A 0.5-1.0 g aliquot of alloy was dissolved in 3 ml of concentrated sulfuric acid and 10 ml of nitric acid. After cessation of the turbulent reaction the solution was evaporated to the appearance of thick SO_3 fumes; it was then cooled, and diluted with water. The solution was transferred to a 100 ml standard flask and made up to the mark with distilled water. An aliquot of this solution containing 2-20 mg of molybdenum was transferred to a 250 ml conical flask and 4 g of urea added; the solution was next heated to the boil and 15 ml of hydrazine sulfate added; the solution was boiled again for a further 2-3 minutes and the procedure outlined above then followed, i.e. EDTA-Na was added and excess of it titrated with zirconium sulfate. Results of these determinations are given in Table 5.

Specially conducted experiments showed that trivalent iron, zirconium, hafnium, phosphates, flurides, oxalates, citrates, and tartrates interfere with determination of molybdenum by the given method.

The method suggested permits determination of the molybdenum content of the solution obtained after decomposition of test material to be carried out in 20 min.

SUMMARY

The molar extinction coefficient of solutions of the compound of quinquevalent molybdenum with ethylenediaminetetracetic acid $(MoO_2)_2H_2Y$ is 363 ± 8 at 387 mμ, while the complex formation constant is $1.75 \pm 0.52 \times 10^{11}$ at a confidence level of 0.95.

A variant which has been developed for the complexometric determination of quinquevalent molybdenum is based on complexing the molybdenum with EDTA-Na, and titrating excess of the latter with zirconium sulfate solution, using xylenol orange as indicator.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION 3. PHOTOMETRIC DETERMINATION OF URANIUM IN ORES AND THEIR PROCESSED PRODUCTS BY MEANS OF ARSENAZO I*

V. F. Luk'yanov, L. M. Moiseeva, and N. M Kuznetsova

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Arsenazo I (benzene-2-arsonic acid-<1-azo-2>-1,8-dihydroxy-naphthalene-3,6-disulfonic acid) forms with the uranyl ion at pH 4-8 a blue colored complex which is readily destroyed by hydrogen peroxide [1]. Many elements react with arsenazo under these conditions, and accordingly, in order to determine uranium in ores, it must be isolated in a pure state, free from impurities [2].

Table 1. Determination of Uranium in ores after Its Separation by Partition Chromatography

Uranium content, %		Found by the sug. method
No. of determinations	Specified value	
0,083±0,001	0,083±0,001	10
0,237±0,006	0,240±0,001	10
0,560±0,011	0,570±0,002	10
0,059±0,004	0,061±0,001	10
0,070±0,001	0,069±0,001	10

Table 2. Determination of Uranium in Processed Products from Uranium Ores

Uranium content %		Uranium content %	
By the suggested method	By other meth.	By the suggested method	By other meth.
0,019	0,019	0,012	0,013
0,013	0,014	0,013	0,012
0,013	0,015	0,013	0,015
0,012	0,012	0,012	0,010

In the present article a description is given of a photometric determination of uranium with arsenazo I, after a preliminary separation of uranium from the impurities by a partition chromatographic method and by ion exchange on SG-1 carboxyl resin.

Burstall and Wells [3] were the first to describe a partition chromatographic method for purifying uranium [3]. We used a variant of this method suggested by Markov [4]. In this variant the carrier is chemically pure silica gel, while the stationary phase is a saturated solution of ammonium nitrate acidified with nitric acid to an acidity of 0.5 N with respect to nitric acid, and the mobile phase is ethyl ether also acidified with nitric acid to a value of 0.5 N.

Using a 6-7 cm column of the purifying layer (silica gel soaked with the stationary phase) and an ether throughput of 1-2 ml/min, only 40-45 ml of ether is required for separating the uranium completely from impurities, in contrast to the 150-200 ml recommended in Burstall and Wells' method. In the absence of interfering anions (F^-, Cl^-, SO_4^{2-}, and other ions which complex uranium into a complex which is insoluble in ether) only vanadium, in the form of its red colored peroxide compound, moves with the uranium at an appreciable velocity along the column. The rate at which vanadium moves along the column is, however, low compared with that of uranium, and does not interfere with determination of the latter. At high vanadium contents of samples Markov recommends its reduction with hydrazine nitrate. Chemically pure silica gel** with a particle size of 0.5 mm was calcined at 450° for one hour before use. A saturated solution of ammonium nitrate which was 0.5 N with respect to nitric acid (solution I) was prepared by adding 50 ml of concentrated nitric acid per liter of a saturated ammonium nitrate solution. The solution obtained was titrated with alkali and its acidity adjusted to 0.5 N either by addition of acid or a saturated solution of ammonium nitrate. To prepare a similar solution (solution II), with an acidity of 1.15 N with respect to nitric acid, 115 ml of concentrated nitric acid was added per liter of saturated ammonium nitrate solution. Diethyl ether, 0.5 N with respect to nitric acid, was prepared by shaking equal volumes of ether and solution II in a separating funnel for 2-3 min.

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*For communication 2, see Zh. analit. khimii 16, 60 (1961).

** The silica gel was prepared according to Markov and Volkova's method [4].

Uranium was determined in ores as follows. An aliquot of sample containing 50-100 μg of uranium was decomposed with nitric acid.

When other methods are used for decomposing test material, anions which interfere with extraction of uranium must be removed.

Anions of volatile acids were removed by evaporating the sample four to five times with nitric acid; it was freed from other anions by precipitating the hydroxides and subsequently dissolving these in nitric acid.

After the sample had been decomposed and the insoluble residue had been removed, the solution was evaporated to the damp salt state. 0.5 ml of solution I was added, followed by 1-2 ml of silica gel, which, after mixing with the solution should retain its friable character. Otherwise, a little more of it should be added.

Uranium was separated from impurities in the chromatographic column. Two ml of solution I and 6-7 ml of silica gel were first introduced into the column. Next the reducing layer of 1-1.5 ml of silica gel saturated with 5% hydrazine nitrate was inserted, followed by the partitioning layer—silica gel saturated with the test solution. Ether was passed through a column prepared in this way at the rate of 1-2 ml/min. The ethereal solution of uranyl nitrate issuing from the column was collected in a beaker containing 10-15 ml of water. Completeness of elution of uranium was controlled by a luminescence method. The ether was removed by careful evaporation on a water bath and the uranium in solution determined photometrically with arsenazo I [5]. For this purpose the solution was transferred to a 50 ml standard flask, in which it was neutralized with ammonia, using methyl red as indicator; two drops of HCl (1:1), 1 ml of 25% urotropine solution, and 2 ml of 0.1% arsenazo I solution were added, and the volume made up to the mark with water. After 10-15 min the optical density of the soltuion was measured on a FÉK-M photocolorimeter fitted with red filter and using a 2 cm cell.

The reference solution used was one containing all the reagents apart from uranium. Ten drops of 30% H_2O_2 was added to the cells containing the test and reference solutions, the solutions were stirred and the optical density measured again. The uranium content was determined from a calibration curve constructed in a similar way using solutions with 20, 40, 60, 80, and 100 μg uranium in 50 ml of solution.

Results for the determination of uranium in a series of ore standards and processed products from uranium ores are shown in Table 1 and 2.

The comparatively high sensitivity of the method permits it to be used for determining small amounts of uranium (0.001-0.1%) with sufficient accuracy in ores, in those cases where other methods do not give reliable results. Nevertheless, because of the necessity of using ether, and the need for specially prepared silica gel, the method has limited possibilities for its wide application in plant laboratories and for control purposes.

We have tried to overcome the disadvantages of the method described above for purifying uranium by using ion exchange on the carboxyl ion exchange resin SG-1 for this purpose.

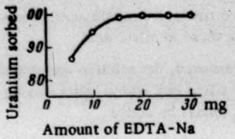
Comparatively little work has been devoted to the study of the behavior of uranium on cation exchange resins, and its use for analytical purposes. Ishimori and Okuno [6] have described the behavior of uranium on the strongly acid cation exchange resin Dowex 50. Kennedy and Davies [7] used a phosphoric resin for separating uranium from heavy metal; Fodor [8] used the cation exchange resin Amberlite URC-50 for separating uranium from impurities, using sodium ethylenediaminetetracetate (EDTA-Na). A similar method has been described by Ryabchikov, Palei, and Mikhailova [9] in which the cation exchange resin KU-2 was used. The principle of the method consists in complexing elements which interfere with the quantitative determination of uranium by means of EDTA-Na, followed by selective sorption of the uranium with a cation exchange resin. Our work consisted in establishing the conditions for selective sorption of uranium by the carboxyl resin SG-1 from solutions containing EDTA-Na.

7-8 ml of resin SG-1 (particle size 0.4-0.6 mm) in the swollen state was introduced into a chromatographic column with a diameter of 10 mm and was treated with 10% HCl until the eluate gave a negative reaction for Fe^{III}, and was finally washed with distilled water until the eluate gave a negative reaction for Cl^-. A column prepared in this way was kept under distilled water.

A standard solution of uranyl nitrate with a concentration of 1 mg/ml and a 5% aqueous solution of EDTA-Na were used in our work. 10% HCl was used for eluting the uranium from the column.

The method of investigation consisted of the following. A solution of a definite pH value containing uranium, a foreign element, and the requisite amount of EDTA-Na was passed through the resin column at a rate of about

1 ml/min. The column was then washed with 100-150 ml of distilled water and the uranium eluted from the column by passing 50-75 ml of HCl, and then distilled water until the total volume of eluate was 100 ml (the eluate was collected in a 100 ml standard flask). The uranium content of the eluate was determined as described above.



The relation between sorption of uranium from solutions containing PO_4^{3-}, and the amount of EDTA-Na. 5 mg of uranium and 10 mg of phosphorus (molar ratio 1:17) were taken for each determination.

Experiments on the sorption of uranium from solutions with varying pH values, in the presence of EDTA-Na, showed that sorption of 10 mg of uranium is quantitative only at pH≥ 3.

The pH limit at which the column operates can be lowered to 1.5 when the uranium is sorbed on the resin in the NH_4-form. The resin was converted to its NH_4- form by washing it with 200 ml of 0.1-0.5% ammonium nitrate. This same solution can be conveniently used for washing the column after sorption. The resin does not swell under these conditions, as occurs when the column is washed with water.

The effect of a series of ions: PO_4^{3-}, SO_4^{2-}, MoO_4^{2-}, VO_3^-, F^-, Fe^{III}, Al, Ti, Ca on the sorption of uranium was studied.

MoO_4^{2-} and WO_4^{2-} do not interfere with uranium sorption. When vanadium is present, sorption of 10 mg uranium is quantitative only when the pH is 3.5-4.5 and in the presence of a sufficient excess of EDTA-Na (not less than 100 mg per 1 mg uranium). The effect of other elements was only studied over the pH range 3.5-4.5.

Completeness of uranium sorption from solutions containing PO_4^{3-} ions also depends on the EDTA-Na concentration of the solution (see diagram).

Table 3. Determination of Uranium in Ores after Its Sorption on SG-1 Cation Exchange Resin

Uranium content, %		By the specified method	Uranium content, %		By the specified method
No. of determinations	Specified content		No. of determinations	Specified content	
0,070±0,001	0,069±0,001	18	0,083±0,001	0,081±0,005	8
0,103±0,002	0,102±0,001	15	0,059±0,004	0,059±0,001	15
0,560±0,011	0,557±0,004	11	0,220±0,01	0,214±0,002	5

Since we did not have to deal with samples containing much phosphorus, its effect at molar ratios to uranium greater than 17:1 was not examined.

SO_4^{2-} ions start to interfere at a molar ratio of UO_2^{2+} : SO_4^{2-} = 1:200, while F^- starts to interfere at a molar ratio of 1:10, even when an appreciable excess of EDTA-Na is present. Interference from elements of the second group on the sorption of uranium and on its subsequent determination with arsenazo I was not observed.

Uranium was determined in ores as follows. A 0.5 g aliquot of sample (for uranium contents of 0.01-0.1%) was decomposed with hydrochloric acid and hydrogen peroxide. After removal of the insoluble residue, 15-20 ml of 5% EDTA-Na solution was added and the solution alkalinified with ammonia until the color of the solution changed (pH 7). When the solution was turbid at this stage it was acidified again, and some additional ml of EDTA-Na solution added; it was finally alkalinified to a pH of 3.5-4.5 using an external universal indicator; this solution was passed throuhg a column of SG-1 resin in the NH_4-form at the rate of 1 ml/min. The column was next washed with 200 ml of 0.1-0.5% ammonium nitrate solution at the rate of 2-3 ml/min and the uranium eluted with 75 ml of HCl (10% by volume), the eluate being collected in a 100 ml standard flask. The volume of the solution was made up to the mark with distilled water which had been passed through the same column, and the uranium content determined by means of arsenazo I.

The column was restored to its working state by passing ammonium nitrate solution through it until the pH of the solution issuing from the column was 3.5-4.5. The method is simple to carry out and allows 10-15 samples to be dealt with simultaneously. Table 3 contains results for the determination of uranium in a series of ore standards.

SUMMARY

A photometric method has been developed for the determination of uranium in ores, and in processed products from these ores by means of arsenzao I. Uranium is removed beforehand from impurities either by a partition chromatographic method, or by ion exchange on the cation exchange resin SG-1 in the presence of EDTA-Na.

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PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COBALT AS COBALT (III) DIETHYLDITHIOCARBAMATE

K. P. Stolyarov

A. A. Zhdanov Leningrad State University

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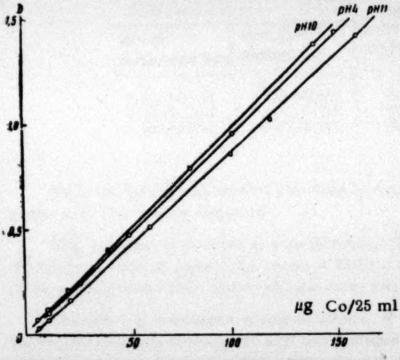
There are numerous and diverse methods in existence for the photometric determination of small amounts of cobalt. The ones most widely used are those based on formation of innnercomplex (and salt form) compounds with organic reagents. Most of them, however, do not solve the problem of determining cobalt in the presence of nickel, which has similar chemical properties. Introduction of additional operations for removing nickel complicate the methods appreciably and render them unsuitable.

We have tried to develop a rapid, accurate, and sensitive method for the determination of small amounts of cobalt in the presence of large amounts of nickel, copper, manganese, zinc, and other elements. The method is based on the results of a study of the chemical interaction of sodium diethyldithiocarbamate with the ions of various metals and the behavior of the interaction products toward organic solvents, in particular, to carbon tetrachloride.



It is known [1-5] that the solubility of metal diethyldithiocarbamates in organic solvents is strongly dependent on the pH of the aqueous solution. By selecting the pH of the solution and using various masking agents it is possible to extract various diethyldithiocarbamates selectively. Bode [3,4] as a result of a systematic study of the extractability of diethyldithiocarbamates by various organic solvents in the presence of masking agents, and in their absence, established that the diethyldithiocarbamates of Ag, Bi,Co, Cd, Cu, Hg, Ni, Pb, Pd and Tl are extracted at pH's greater than 11, while of these elements Ag, Bi, Hg, Pd, and Tl do not interact with sodium ethylenediaminetetracetate (EDTA-Na). Ni and Mn form the most stable complexes with EDTA-Na, so that they cannot be extracted from solution in the presence of this masking agent, whatever the pH, while Co, Fe, and Zn are extracted at pH< 6.

On shaking a solution of Co^{II} with diethyldithiocarbamate and CCl_4 in air, the Co^{III} diethyldithiocarbamate which is always formed is quantitatively extracted from solution at pH 4-11. The solution of Co^{III} diethyldithiocarbamate in CCl_4 has two absorption maxima at 323 and 367 mμ, which can be used for the quantitative determination of cobalt.

The selectivity of diethyldithiocarbamate methods can be enhanced by replacing one of the carbamates by others as a function of their stability. Thus divalent mercury almost quantitatively replaces many elements (with the exception of nickel) from their diethyldithiocarbamates, while cobalt is not replaced[6].

In order to establish the possibility of determining cobalt photometrically as its diethyldithiocarbamate in CCl_4• a preliminary series of experiments was carried out which showed that Co^{III} diethyldithiocarbamate passes

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•All measurements were made on a FÉK-N-54 photocolorimeter fitted with filters, λ_{max} = 365 mμ, in 1 cm cells.

almost completely into the organic phase after shaking for two minutes with CCl_4, and that its solution is stable for 3 hr. During extraction in a separating funnel 20 ml of buffer mixture with pH 10.17•, 0.5 ml of cobalt salt solution (50 µg), and 1 ml of 0.5% sodium diethyldithiocarbamate were mixed and shaken with 20 Ml CCl_4. Since extraction of metal diethyldithiocarbamates is strongly dependent on pH, experiments were carried out to establish the optimum pH range for extraction of cobalt diethyldithiocarbamate. For this purpose the optical density of extracts with varying pH (4, 10, 11)•• and increasing cobalt contents were determined. As the diagram shows, maximum extraction is observed at pH 4-10; over this range the extent of extraction is almost the same. The fact that the curve is linear indicates that solutions of Co^{III} diethyldithiocarbamate in CCl_4 conform to Beer's law throughout the whole cobalt concentration range studied (0 - 150 µg in 25 ml). The sensitivity is 0.2 µg cobalt in one ml.

Table 1

Ion	Me + DDTC - Na		Me + DDTC-Na + EDTA-Na		Ion	Me + DDTC - Na		Me + DDTC-Na + EDTA-Na	
	pH 4	pH 10	pH 4	pH 10		pH 4	pH 10	pH 4	pH 10
Co^{2+}	+	+	+	—	Cr^{3+}	Wkly.	—	—	—
Ni^{2+}	+	+	Weakly	—	Al^{3+}	—	—	—	—
Mn^{2+}	+	+	»	—	As^{V}	—	—	—	—
Fe^{2+}	+	+	+	—	Ca^{2+}	—	—	—	—
Zn^{2+}	+	+	+	—	Mg^{2+}	—	—	—	—
Hg^{2+}	+	+	+	+	Ti^{IV}	—	—	—	—
Cu^{2+}	+	+	+	+	V^{V}	+	—	—	—
Bi^{3+}	+	+	+	+					

To confirm our conclusion on the completeness of extraction of cobalt over the pH range 4 to 10, we used the radioactive isotope of cobalt Co^{60} with a half-life period of 5.24 years. The radioactivity of the Co^{60} solution was measured on a type B apparatus with a γ-counter. Proper functioning of the apparatus before use was checked on a standard uranium sample. Measurements were made in a quartz cell which was fitted directly into the counting tube. The counter and cell were protected with a lead "chamber" with 44 mm thick walls. Extraction was carried out as described above. These experiments showed that the extent to which cobalt is extracted at pH 10 is 99.66%, while at pH 11 it is only 76.8%. A similar result was obtained at pH 4.

In order to establish to what extent the diethyldithiocarbamates of accompanying elements is extracted with CCl_4, and to establish the conditions for eliminating interference from these elements on cobalt determination, we carried out two series of experiments at pH 4 and 10. One series of experiments was carried out to study the interaction of various metal ions with sodium diethyldithiocarbamate, and the other with sodium diethyldithiocarbamate in the presence of EDTA-Na. The results obtained are given in Table 1.

In addition, we checked on the substitution (replacement) series. Twenty ml of buffer solution with pH 4 was introduced into a separating funnel; this was followed by 0.5 ml of a solution of a cobalt salt (or known amounts of the solutions of the salts of other elements), and 2 ml of 0.5% sodium diethyldithiocarbamate, and the cobalt diethyldithiocarbamate (or the carbamates of the other elements) formed extracted with 10 ml CCl_4 for 2 min. A solution of mercuric acetate (0.5%) was then added and the mixture shaken again for 2 or 4 min. The results obtained are given in Tables 2 and 3.

Table 2

Co intro. µg/25 ml	Hg^{II} intro., ml	Co found µg/25 ml	Error
50	0,5	51,0	+1,0
50	1,0	49,5	—0,5
50	1,5	52,7	+2,7
50	2,0	49,0	—1,0

Table 3

Element	Max. amt. of element replaced by 2 ml of 0.5% Hg^{II} sol., µg	Shaking time, min
Ni	400	4
Ni	600	2
Mn	400	4
Mn	600	2

•A mixture of equal volumes of 0.1 M sodium carbonate and 0.1 M hydrochloric acid.

•• The solutions were treated in the same way as that described above, except that the reference solution (CCl_4) was treated in the same way as the cobalt salt solution.

Table 4

Introduced, μg/25 ml					Co found μg	Error μg	Introduced, μg/25 ml					Co found μg	Error μg
Fe	Cu	Mn	Ni	Co			Fe	Cu	Mn	Ni	Co		
			4000	5	6	+1		800		4000	100	98	—2
			4000	25	27	+2		1000		4000	100	93	—7
			4000	50	52,5	+2,5	600			4000	50	50,5	+0,5
			4000	100	97	—3	800			4000	50	58,5	+8,5
		4000		50	46,8	—3,2	600	800		4000	50	50,5	+0,5
		4000		100	99	—1	600	800	4000		50	46,5	—3,5
		4000		140	138,5	—1,5	600	800	2000	2000	50	50,5	+0,5
		2000	2000	60	62	+2							

Table 5

Taken, μg/25 ml					Co found, μg	Error μg	Taken, μg/25 ml					Co found μg	Error μg
Mn	Cu	Ni	Fe	Co			Mn	Cu	Ni	Fe	Co		
			4000	5	3	—2		400		4000	50	55	+5
			4000	50	52,5	+2,5		200		4000	50	52,5	+2,5
			4000	140	139,5	—0,5	400			4000	50	55,5	+5,5
		400	4000	50	56	+6	200			4000	50	48	—2
		200	4000	50	52	+2	200	200	200	4000	50	52	+2

Table 6

Taken, μg /25 ml					Co found μg	Error μg	Taken, μg /25 ml					Co found μg	Error μg
Mn	Fe	Ni	Cu	Co			Mn	Fe	Ni	Cu	Co		
			3000	50	50,5	+ 0,5			200	3000	50	53	+ 3
			3000	130	132	+ 2	200		200	3000	50	52,5	+ 2,2
			4000	50	38,5	—11,5	200	200	200	3000	0	0	0

Table 7

pH	Taken μg/25 ml		Optical density, D	pH	Taken μg/25 ml		Optical density, D
	Co	Zn			Co	Zn	
10	50	0	0,48	4	50	5000	0,29
10	50	5000	0,08	4	50	4000	0,40
4	50	0	0,48	4	0	4000	—0,09

As the results in Table 1 show, on adding sodium diethyldithiocarbamate and EDTA-Na to the test solution, and changing the pH from 10 to 4, small amounts of cobalt can be determined in the presence of many elements. The effect of nickel and manganese, which, despite altering the pH of the medium and adding EDTA-Na, are partially extracted as their carbamates with cobalt, can be eliminated, as is evident from the results given in Tables 2 and 3, by replacing them from their carbamates by mercuric salts. By using such a technique, not one of the elements which we studied hardly affects determination of cobalt.

Determination of Cobalt in the Presence of Large Amounts ofNi and Mn is based on the fact that Co, Mn, and Ni are masked by EDTA-Na at pH 10, and thereby can be completely separated from copper, bismuth, and other elements. Subsequently, by altering the pH of the medium from 10 to 4, cobalt diethyldithiocarbamate is extracted. During this stage iron and some nickel and manganese are also extracted. Their influence can, however, be eliminated by replacing them with Hg^{2+} ions,with formation of colorless Hg^{II} diethyldithiocarbamate, while Co^{III} is not extracted under the same conditions.

Table 8

Intro. μg/25 ml		Co found μg	Error μg
Zinc	Cobalt		
5000	0	0	0
5000	5	5,5	+0,5
5000	25	24,0	−1,0
5000	100	101,0	+1,0
5000	140	136,5	−3,5

Table 9

Sample No.	Specified Co content, %	Co found, %	Mean value, %
1	0.78	0.75 ; 0.78	0.77
2	0.025	0.023 ; 0.021 ; 0.024	0.023
3	0.015	0.018 ; 0.014 ; 0.014	0.015
4	0.014	0.013 ; 0.012 ; 0.012	0.012

When EDTA-Na is present in solution together with sodium diethyldithiocarbamate, simultaneous formation of cobalt carbamate and complexonate is possible, since they possess almost equal stability. The stability of the carbamate is somewhat higher, so that at pH< 6 cobalt complexonate can change into its carbamate in the presence of a sufficient excess of sodium diethyldithiocarbamate. Accordingly, on isolating cobalt with sodium diethyldithiocarbamate in the presence of EDTA-Na, a considerable excess of the latter is necessary. It was established that 4 ml of a 1% solution of sodium diethyldithiocarbamate is necessary for masking 4 mg nickel and 150 μg cobalt.

On the basis of the results of the experiments described above cobalt was determined as follows. Four ml of a 1% solution of EDTA-Na and solutions containing known amounts of cobalt and other elements were introduced into a separating funnel. After shaking for two minutes 16 ml of buffer solution (pH 10), 4 ml of 0.5% sodium diethyldithiocarbamate solution, and 1 ml of glacial acetic acid were added, and extraction carried out for 2 min with 10 ml CCl_4. Two ml of a 0.5% solution of merucric acetate solution was then added and the funnel shaken a further 4 min. The extract was transferred through a dry filter into a 25 ml standard flask. The extraction was repeated, the second extract combined with the first, and the volume made up to the mark with CCl_4. After mixing, the optical density was measured in a cell with a path length of 1 cm at 365 mμ, relative to the extract obtained from a solution not containing cobalt which had been and treated in the same way as the test solution. When copper and metals similar to it were present, after addition of the buffer solution, 2 ml of 0.5% sodium diethyldithiocarbamate solution was added. The precipitate of the carbamates of copper and the other elements were removed by extraction with CCl_4. Determination of cobalt was then carried out as described above.

From the results obtained (Table 4) it is clear that iron, copper, nickel, and manganese do not interfere with the determination at ratios of Co:Ni:Mn = 1:800;800; Co:Cu = 1:160, and Co:Fe = 1:120. Microamounts of Ag, Bi, Cd, and Pb do not interfere (according to the results in Table 1).

Determination of Cobalt in the Presence of Large Amounts of Iron. As previous experiments have shown, during determination of cobalt with sodium diethyldithiocarbamate, iron is replaced by mercuric ions only at ratios of Co:Fe = 1:120.

Pyatnitskii [7] has shown that at pH 10 iron is masked by tartaric or citric acid. Under these conditions cobalt is not affected. A check which we carried out showed that the pH of the medium must be strictly controlled. This limits the possibility of using this method of masking iron. Pribil et al [8] used thoron (pyrocatecholdisulfonic acid) as a masking agent. We used pyrocatechol, which readily masks iron in weakly ammoniacal media, for this purpose. Determination was carried out as follows. Four ml of 1% pyrocatechol solution and the test solution containing known amounts of cobalt and interfering elements were introduced into a separating funnel. Ammonia was then added dropwise until the solution had a red color, 15 ml of buffer solution (pH 10) and 4 ml of 0.5% sodium diethyldithiocarbamate were then added. The solution was next extracted with 10 ml of CCl_4 for 2 min. The extract was transferred to another funnel containing 15 ml of buffer solution (pH 10) and 2 ml of 0.5% mercuric acetate solution, and the funnel shaken for 2 min. The extract which had been freed from impurities was filtered through a dry filter into a 25 ml standard flask. The extraction was repeated. The combined extracts were made up to the mark with CCl_4, and the optical density measured in a 1 cm cell at 365 mμ, relative to CCl_4 treated in the same way. Results of these determinations are given in Table 5.

By using pyrocatechol it is possible therefore to determine cobalt in the presence of iron, manganese, copper, and nickel.

Determination of Cobalt in the Presence of Large Amounts of Copper. Copper, in contrast to cobalt, does not interact with EDTA-Na, and can be precipitated with sodium diethyldithiocarbamate at pH 10 and removed by subsequent extraction with CCl_4; under these conditions cobalt remains in the aqueous solution in which it is determined. In those cases where the solution also contains, in addition to copper, elements which, like cobalt, form complexonates, these elements are replaced from their carbamates by means of a mercuric salt. The determination was carried out as follows. Two ml of a 1% solution of EDTA-Na, solutions containing known amounts of cobalt and other elements, 17 ml of buffer solution, and 2 ml of a 2% solution of sodium diethyldithiocarbamate were mixed in a separating funnel. Copper carbamate was then extracted with CCl_4. Extraction was repeated until the extract obtained was colorless. A further 2 ml of 2% sodium diethyldithiocarbamate solution was then added, and the pH adjusted from 10 to 4 by adding 1 ml of glacial acetic acid. The colored precipitate was extracted with 10 ml of CCl_4. Two ml of 0.5% mercuric acetate solution was added and the funnel shaken for 2 min. The purified extract was transferred through a dry filter into a 25 ml standard flask. The extraction was repeated. The volume was made up to the mark with CCl_4 and the optical density measured relative to an extract obtained from a blank run. The results obtained are given in Table 6. It follows from these that cobalt can be determined in the presence of 600 times its amounts of copper and 40 times its amount of nickel, iron, and manganese.

Determination of Cobalt in the Presence of Large Amounts of Zinc. Zinc, like cobalt, in the presence of EDTA-Na is precipitated by sodium diethyldithiocarbamate at $pH < 6$, and is extracted together with cobalt. Nevertheless, since zinc carbamate does not exhibit appreciable absorption in the ultraviolet, cobalt can be determined in the presence of zinc without a preliminary separation of these elements. Our experiments have shown, however, that in the presence of zinc, the optical density of the solution decreases (Table 7), presumably because of the interaction of zinc with the free sodium diethyldithiocarbamate in solution, as a result of which the optical density of the reference solution increases relatively (since sodium diethyldithiocarbamate exhibits appreciable absorption at 365 mμ, the results for cobalt are low). Accordingly, zinc must either be removed before determination, or must be replaced by addition of a mercuric salt solution; for this purpose extraction must be carried out at pH 4, since at pH 10 the basic zinc salt formed as the result of hydrolysis adsorbs the cobalt.

On the basis of experiments which we carried out, the following analytical procedure can be suggested. Nineteen ml of buffer solution (pH 4) and a solution containing cobalt and zinc are introduced into a separating funnel. Four ml of a 2% solution of sodium diethyldithiocarbamate is then added and the mixture extracted with about 10 ml of CCl_4; having added 2 ml of 0.5% mecuric acetate solution, the funnel is shaken up again for a further 2 min. The extract is next transferred through a dry filter into a 25 ml standard flask. Extraction is repeated. The extracts are combined and their volume made up to the mark with CCl_4; the optical density is then measured relative to CCl_4 treated in the same way. Results of cobalt determination are given in Table 8.

In order to check on the method, we analyzed samples of nickel metal (sample No. 1), copper-zinc sulfide ores (samples Nos. 2 and 3), and an ore with a high content of rare earths (42.2%; sample No. 4).

Determination of Cobalt in Nickel Metal. An aliquot was dissolved on heating in a mixture of acids [10 ml HCl (1:1) + 5 ml HNO_3]. After evaporating to dryness the residue was dissolved in hot water, the solution transferred to a 100 ml standard flask, and its volume made up to the mark with water. A 2 ml aliquot of this solution was pipetted into a separating funnel and cobalt determined by the procedure outlined (determination of cobalt in the presence of nickel and manganese). The results are given in Table 9.

Determination of Cobalt in Rocks. An aliquot of 0.5-1.0 g was decomposed with a mixture of hydrochloric and nitric acids on heating. The solution was diluted with an approximately equal volume of water; it was then cooled, and after silica was filtered off was evaporated to dryness. The dry residue was moistened with a small amount of hydrochloric acid, and again evaporated to dryness to remove the nitric acid completely. The residue was dissolved in 8-10 ml of 6 N hydrochloric acid and the iron removed by extraction with 10 ml of ether saturated with 6 N HCl. The ethereal layer was discarded. The aqueous layer was evaporated to the moist salt stage, the salts were dissolved in hot water and the solution obtained filtered into a 50 ml standard flask. An aliquot (5-10 ml) was transferred to a separating funnel, and 4 ml of EDTA-Na and 11 ml of buffer solution (pH 10) added; ammonia was finally added dropwise until the pH was 10 (indicator paper). Analysis was subsequently carried out according to the procedure outlined for the determination of cobalt in the presence of nickel, manganese, and copper (samples 2 and 3), or by the procedure given for the determination of cobalt in the presence of copper (sample No. 4): Since sample No. 4 contained 42.2% of rare earths in addition to iron, copper, zinc, and calcium, the rare earths were removed as their oxalates [9] before removing the iron. As the results given in Table 9 show, the suggested method gives completely satisfactory results.

SUMMARY

A study has been made of the conditions necessary for the photometric determination of small amounts of cobalt in the form of Co (III) diethyldithiocarbamate at λ_{max} = 365 mμ. The optimum pH range for extracting cobalt carbamate with carbon tetrachloride has been established by means of Co^{60} (pH 4.0 - 10.0).

A photometric method has been developed for the determination of small amounts of cobalt in the presence of large amounts of nickel, manganese, copper, iron, and zinc, in which the cobalt is determined in the form of a solution of cobalt (III) diethyldithiocarbamate in CCl_4. The sensitivity of the method at λ_{max} = 365 mμ is 0.2 μg Co/ml. Solutions conform to Beer's law over the range 0 - 150 μg/25 ml. Satisfactory results have been obtained during the determination of cobalt in samples of nickel metal and rocks.

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DETERMINATION OF FREE NITRIC ACID IN URANYL NITRATE TRIBUTYLPHOSPHATE SOLUTIONS

V. M. Mikahilov

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The absence of analytical methods of determining free nitric acid in organic solvents (a mixture of tributyl phosphate with CCl_4 or saturated high boiling hydrocarbons-SHBH *) compels the research worker to transfer the contents of the organic phase into an aqueous solution, in which the free nitric acid is determined by potentiometric or conductometric titration. Such a method, however, is not justified, because of the long time taken to carry it out, but mainly because of the appreciable errors which arise during determination of acidity, since in the final result this reduces to the old problem of determining acidity in the presence of one or several hydrolyzable salts [1-7].

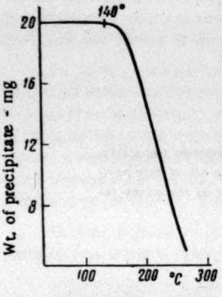

Fig. 1. Thermogravigram of acridine nitrate.

The use of complexing agents [2,3] and heavy metal salt precipitants [6,7] appreciably lengthens the course of an analysis and does not lead to the desired effect in the case of low concentrations of free acid. Indirect methods of determining acidity (the use of cation exchange resins in the H-form, H_2O_2, etc) are also not free from the disadvantages listed above.

We have tried to use the simplest aliphatic and cyclic amines for the detection and quantitative determination of nitric acid directly in tributylphosphate solutions.

During the isolation of amines from aqueous or mixed (water and organic solvent) solutions in organic syntheses, wide use is made of neutralization reactions leading to the formation of sparingly soluble salts of an organic base and a mineral acid. Hydrochloric acid is most frequently used for this purpose, but, generally speaking, the choice of acid depends to a considerable extent on the type of amine, and on the medium in which it is found. It is obvious, that if, on the other hand, the mineral acid is in the organic phase, then its presence can be detected by means of amines. Information has been published [8] to the effect that salts of aliphatic amines of high molecular weight (of the order of 250-600) are considerably more soluble in organic solvents of low polarity, and are used during the extraction separation of heavy metals [8,9]. Accordingly, we have only examined the simplest and most readily available representatives of the class of aliphatic and cyclic amines.

Although tributylphosphate solutions of uranyl nitrate always contain some water in the form $TBP \cdot H_2O$ [10] it might be expected that the addition of a very weak organic base to such solutions should not lead to chemical processes related to the hydrolysis of uranyl nitrate.

Qualitative tests (Table 1) showed that many of the amines tested form precipitates with the nitric acid present in tributylphosphate solutions. The simplest representatives of the aromatic amines proved to be good precipitants. Of these, the one of greatest practical interest was acridine (2,3-dibenzopyridine), the sensitivity of which to HNO_3 proved to be highest (the usual weighting effect of an organic molecule in a homologous series), while its salt form — acridine nitrate — is very stable under ordinary conditions. Thermogravimetric study showed that this compound (Fig. 1) can be heated up to 120° without suffering appreciable decomposition or volatilization; in addition, it was established that it does not possess any appreciable hygroscopicity.

The composition of the precipitate was determined by conductometric and indicator titration, and also gravimetrically.

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* SHBH — saturated high boiling hydrocarbons.

Table 1

Amine*(about 0.01 M solution in CCl_4)	20% tributylphosphate in CCl_4 containing 0.05 M HNO_3	20% tributylphosphate in SHBH containing 0.05 M HNO_3
Ethylamine	–	White precipitate
Diethylamine	White precipitate	" "
Allylamine	No precipitate formed	–
Aniline	White precipitate	White precipitate
p-Anisidine	" "	" "
α, β-Naphthylamines	" "	" "
Pyridine	" "	" "
Quinoline	" "	" "
Quinaldine	" "	" "
Acridine	Yellow precipitate	Yellow precipitate
Diphenylamine	No precipitate formed	No precipitate formed
Benzidine	White precipitate	White precipitate
Nitron	No precipitate formed	No precipitate formed

*5-7 ml of a carbon tetrachloride solution of the amine was added to about 1 ml of tributylphosphate solution containing HNO_3 in each case.

In the first instance an accurately weighed aliquot of acridine nitrate, obtained by precipitation in tributylphosphate solutions, was taken, and the amount of nitric acid present calculated on the basis of the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$. The aliquot was then dissolved in a mixture of $H_2O - CH_3OH$ (4:1) and titrated with an aqueous alkali solution. The ecuivalence point was clearly defined both when visual titration with and without an indicator (phenolphthalein) was used.

In the second instance, knowing the exact concentration of nitric acid in a 4% solution of tributylphosphate (CCl_4 and SHBH were used for diluting the tributylphosphate), it was precipitated as acridine nitrate by adding an excess of a solution of acridine in CCl_4. The precipitate was filtered off through a No. 3 or No. 4 crucible, washed with carbon tetrachloride, dried at 90°, and weighed.

As a result of these experiments it was established that addition of acridine to acid (with respect to HNO_3) tributylphosphate leads to formation of a sparingly soluble compound whose composition corresponds to the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$. The solubility of this compound decreases with decreasing percentage content of the tribuylphosphate in the inert solvent (CCl_4, SHBH). Thus the solubility in 5% and 2% solutions of tributylphosphate in CCl_4 is 50 and 20 mg/liter respectively, or in terms of nitric acid 13 and 5.2 mg/liter. At the same time acridine nitrate is almost insoluble in carbon tetrachloride not containing tributylphosphate. Its solubility in solutions of tributylphosphate in SHBH is also dependent to a considerable extent on the tributylphosphate concentration. Accordingly, it is desirable to dilute the test solutions with carbon tetrachloride so that the tributylphosphate content of the latter is not higher than 5%, and then precipitate the nitric acid by adding excess of the free base dissolved in CCl_4. Precipitation experiments (Table 2) showed that gravimetric determination of nitric acid is impossible when the extent to which 20% tributylphosphate solutions is saturated with uranyl nitrate is 50-95%, while the nitric acid content is not greater than 0.02M. On the other hand this is connected with the slight solubility of acridine nitrate in tributylphosphate solution, and on the other hand with the entrainment of some uranyl nitrate in the precipitate, which leads to appreciable (up to 30% relative) errors during gravimetric determination of nitric acid as acridine nitrate. Washing the precipitate on the filter with a 2% solution of tributylphosphate containing about 0.03 M HNO_3 does not always produce the desired effect. It was established that reasonable results could be obtained by applying a correction for the uranyl nitrate entrained in the precipitate. In order to do this a known amount of the precipitate (after the first weighing) was transferred from the porous filter to a porcelain crucible, in which it was weighed; the contents of the crucible were then calcined at 850-900°. The amount of uranyl nitrate which was trapped in the precipitate and determined in this way was then subtracted from the result of the original gravimetric determination (see Table 2).

In some instances (low HNO_3 contents in tributylphosphate solutions) nitric acid can be determined photometrically using the yellow color of acridine in solutions of mineral acids for this purpose.

Table 2. Gravimetric Determination of Nitric Acid in 20% Tributylphosphate Solutions by Means of Acridine*

Expt. No.	Extent to which the tributylphosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3 in sol., mg	HNO_3 found, mg	Deviation from true value	Expt. No.	Extent to which the tributylphosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3 in sol., mg	HNO_3 found, mg	Deviation from true value
1	0	55,5	55,0	−0,5	10	70	55,5	61,6	+ 6,1
2	0	97,0	96,6	−0,4	11***	70	55,5	56,4	+ 0,9
3	5	55,5	55,2	−0,3	12**	90	55,5	67,4	+11,9
4**	5	48,5	48,8	+0,3	13***	90	55,5	57,0	+ 1,5
5	10	25,0	25,3	+0,3	14	90	25 0	31,2	+ 6,2
6**	10	48,5	49,2	+0,7	15***	90	25,0	23,7	− 1,3
7**	30	55,5	56.8	+1,3	16	95	25,0	30,5	+ 5,5
8	30	55,5	56,1	+0,6	17***	95	25,0	25,8	+ 0,8
9	40	55,5	56,2	+0,7					

*The volumes of the original solutions did not exceed 10 ml.

** 20% Solutions of tributylphosphate inSHBH, the remainder in CCl_4.

*** Corrections applied for uranyl nitrate content as a result of gravimetric determinations.

Just as in the case of gravimetric determination, the precipitate on the filter must be washed with a 2% solution of tributylphosphate in CCl_4 containing a small amount of nitric acid, about 0.03 N; subsequently the precipitate is washed with small portions (5-10 ml) of carbon tetrachloride to remove tributylphosphate, and the acridine nitrate then dissolved in 0.1 N HCl. A calibration curve is constructed by using specially prepared soltuions of tributylphosphate with known nitric acid contents; in this way it is also possible to automatically apply corrections for the slight but definite solubility of acridine nitrate in tributylphosphate solutions. The optical density is measured using a blue filter. Since the solutions do not conform to Beer's law over the working part of the calibration curve, a sufficiently large number of points must be taken. Results of photometric determination are given in Table 3.

Table 3. Photometric Determination of HNO_3 on the Basis of the Color of Acridine Nitrate in 0.1 N HCl.

Expt. No.	Extent to which the tributylphosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3, mg	Amt. of test sol., ml	HNO_3 found, mg	Exptl. error (relative)	Expt. No.	Extent to which the tributylphosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3, mg	Amt. of test sol., ml	HNO_3 found, mg	Exptl. error (relative)
1	0	11,6	2	11,7	+1	9	60	5,8	10	5,8	0
2*	0	11,6	4	11,4	−2	10*	25	5.8	10	5,6	−3
3	50	11,6	2	11,6	0	11	0	5,8	20	6,0	+3
4	50	11,6	2	11,4	−2	12	20	5,8	20	5,9	+2
5	75	11,6	4	11,6	0	13 ✓	60	5,8	20	5,6	−3
6*	80	11,6	4	12,2	+5	14	0	1,16	10	1,07	−8
7	0	5,8	10	5,7	−2	15*	5	1,16	10	1,14	−2
8*	5	5,8	10	5,8	0	16	95	1,16	10	1,07	−8

*20% Solutions of tributylphosphate in SHBH, the remainder in CCl_4.

Even smaller amounts of nitric acid (of the order of 0.002-0.0002 M) could obviously be determined nephelometrically directly in tributylphosphate solutions in the presence of uranyl nitrate.

Formation of acridine nitrate is particularly convenient for the qualitative detection of free nitric acid; the limiting dilution is 1:80,000 for 20% solutions of tributylphosphate in SHBH, while the limit of identification is 50 μg. Using this reaction it is possible to detect complex formation(mono- and dialkylphosphates, β-diketones, etc) and solvolysis processes (carboxylic and other organic acids) which occur in tributylphosphate solutions between uranyl nitrate and the compounds indicated, since nitric acid is formed as the result of chemical interaction.

SUMMARY

A new method has been developed for the gravimetric and photometric determination of free nitric acid in tributylphosphate solutions containing varying amounts of uranyl nitrate.

The composition of the compound formed as the result of the interaction of nitric acid and acridine in tributylphosphate solutions corresponds to the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

ELEMENTAL ANALYSIS BY THE "WET COMBUSION" METHOD

COMMUNICATION 3. DETERMINATION OF CARBON AND NITROGEN IN NITRO COMPOUNDS ON ONE ALIQUOT*

A. P. Terent'ev and B. M. Luskina
M. V. Lomonosov Moscow State University
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The "reduced" and "oxidized" forms of nitrogen can be distinguished by their behavior during the oxidation of nitrogen-containing materials. Amines, imines, etc, which liberate ammonia on oxidation with sulfuric acid, contain the reduced form of nitrogen. Materials with azo-, hydrazo-, nitro- and nitroso groups etc, which, on oxidation, liberate nitrogen as the elemental form or nitrogen oxides, can be regarded as compounds which contain the oxidized form of nitrogen.

Determination of Carbon and Nitrogen in Compounds Containing the Oxidized Form of Nitrogen, Using One Aliquot

Test Material	C, %		Difference	N, %		Difference
	Found	Calculated		Found	Calculated	
2-Methyl-3-carbethoxy-4-nitro-5-methoxy-6-methylbenzofurane $C_{14}H_{15}O_6N$	57,15 57,44	57,33	−0,18 +0,11	4,75 4,58	4,78	−0,03 −0,20
2-p-Nitrophenyl-3-carbethoxy-5-methoxybenzofurane $C_{18}H_{15}O_6N$	63,31 63,39	63,34	−0,03 +0,05	3,90 3,93	4,10	−0,20 −0,17
3,5-Dinitrobenzoic acid $C_7H_4O_6N_2$	39,51 39,71	39,63	−0,12 +0,08	13,22 13,09	13,21	−0,01 −0,12
m-Nitrophenol $C_6H_5O_3N$	51,62 51,57	51,80	−0,18 −0,23	9,89 9,93	10,07	−0,18 −0,14
m-Nitroaniline $C_6H_6O_2N_2$	52,02 51,95	52,17	−0,15 −0,22	20,18 20,31	20,28	−0,10 +0,03
p-Aminoazobenzene $C_{12}H_{11}N_3$	72,82 73,11	73,07	−0,25 +0,04	21,62 21,57	21,31	+0,31 +0,26

Methods have been published for the simultaneous determination of carbon and nitrogen by wet combustion. As a rule, they are suitable for compounds in which the nitrogen is in the reduced form [1-3].

We have shown earlier [4] that during combusion of amines, nitriles, indoles, and pyrrolidines with a mixture of sulfuric and chromic acids, carbon is oxidized to carbon dioxide and can be determined gravimetrically, while nitrogen is converted into ammonium sulfate and can be determined as ammonia by distillation after addition of excess alkali. It has also been found that when the reduced and oxidized forms of nitrogen are present at the same time, only the first of these forms is determined.

The wet combustion method, like the Kjeldahl method, without preliminary reduction, is not suitable for the determination of nitrogen in many organic materials. In order to extend the field of application of Kjeldahl's method, various methods have been suggested for the preliminary reduction of materials containing nitrogen in the oxidized form. The following are examples of materials which have been used as reducing materials: glucose [5], hydrogen iodide [6], thiosalicylic acid [7], chromium chloride [8], a hydrochloric acid solution of stannous chloride [9], zinc dust, etc.

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* For communication 2, see Zh. analit. khimii 16, 83 (1961)

In the work described here we have established that the most suitable reducing agent for preliminary reduction of nitro groups is zinc dust in an aqueous solution of sulfuric acid. It was established that in this way it is possible to determine carbon and nitrogen on one aliquot.

Experimental Procedure. A 50-70 mg aliquot was dissolved in 5 ml of dilute (1:2) sulfuric acid, 0.2 g of zinc dust was added and the mixture heated for 10 min at 100°. During this stage nitro groups were reduced and most of the water was removed by evaporation. When the test material did not dissolve in sulfuric acid, the mixture was carefully stirred so that none of the material was lost on the vessel walls. The flask was then cooled and a further 5 ml of concentrated sulfuric acid added; this was followed by 1.5-2 ml of chromic acid and combustion carried out by the method described earlier [4]. The carbon content was determined from the weight of absorbed carbon dioxide in the tube containing askarite. In order to determine the nitrogen, the sulfuric acid solution remaining after combustion was transferred to a flask fitted with a splash head, 50 ml of 40% potassium hydroxide solution was added, and ammonia distilled as usual into 0.1 N acid solution, excess of which was titrated with 0.1 N alkali in the presence of 2-3 drops of methyl red.

The table contains results for the determination of carbon and nitrogen in a few of the materials analyzed, using one aliquot.

The results obtained show that the "wet combustion" method coupled with preliminary reduction is suitable for the analysis of carbon and nitrogen in nitro compounds. It should be pointed out, however, that this method is not suitable, when, during the reduction process, CO or CS_2 is liberated or acetic acid and other volatile organic materials are formed.

It might be expected that azo compounds should be reduced under the conditions indicated, and that on subsequent combustion it should be possible to determine carbon and nitrogen. Analysis of p-aminoazobenzene showed that in fact the results obtained are close to the theoretical values (see table). It is not likely that hydrazones, which are hydrolyzed in acid media with formation of hydrazine salts, can be analyzed in this way.

When the reduced and oxidized forms of nitrogen are present simultaneously, the suggested method could be used for their separate determination. By carrying out combustion after preliminary reduction the total nitrogen content would be determined, e.g.,in p-aminobenzene and m-nitroaniline (see table). By carrying out another combustion without preliminary reduction, only the reduced form of nitrogen would be determined [4]; the oxidized form of nitrogen would then be given by the difference in the two determinations.

SUMMARY

A method has been developed for the determination of carbon and nitrogen in nitro compounds, using one aliquot; it is based on reduction of the nitro group with zinc dust in dilute sulfuric acid, and subsequent wet combustion with chromic and sulfuric acids by a method described earlier. It has been shown that when the reduced and oxidized forms of nitrogen ($-NO_2$ or $-N=N-$) are present simultaneously, the method can be used for their separate determination.

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FLASH COMBUSTION DURING MICRODETERMINATION OF CARBON AND HYDROGEN IN A RAPID STREAM OF OXYGEN

V. A. Klimeva and T. A. Antipova
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR,
Moscow

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We have shown earlier that when test material is decomposed in a tube, the decomposition does not proceed simultaneously throughout the whole mass of test material, but layer by layer, and is accompanied by formation of active fragments of the molecules of the test material [1]. The active products from the decomposition are oxidized in the tube and at the exit from the tube. It is the decomposition products of the test material that pass into the oxidation zone, not the vapors of the material. During decomposition in an empty tube and in a rapid stream of oxygen one cannot on any account leave out the zone of preliminary thermal decomposition. Actually if one examines the various methods used for determination of carbon and hydrogen (Table 1), it becomes clear that combustion with slow evaporation (from a boat) can only be carried out by using excess oxygen, when no other oxidizing agent or catalysts are used, while on carrying out combustion with preliminary decomposition (in a test tube within the combustion tube) reliable results can always be obtained without any supplementary filling of the oxidizing zone.

Table 1

Method	Combustion	Whether the oxidizing zone is packed with oxidizing agents and catalysts	Oxygen flow rate, ml / min
Pregl	In a boat	Yes	4
Niederl and Niederl	"	"	4
Friedrich	In a test tube	"	4
Fedoseeva and Pavlenko	In a boat	"	50
Korbl	"	"	50
Belcher and Spooner*	"	No	50
Belcher and Ingram**	"	"	50
Zabrodina	In a test tube	"	30−50
Korshun and Klimova	"	"	30−50

* The method is not universal.

** The oxidizing zone is lengthened and quartz inserted in it.

In addition, it is known that decomposition in a test tube with preliminary pyrolysis has justified itself, whatever gas stream is used: oxygen [2], hydrogen [3], carbon dioxide [4], and nitrogen [5]. In the first two cases the decomposition can proceed with and without participation of the gas, while nitrogen does not participate, and CO_2 can participate in the decomposition process only by virtue of the fact that at high temperatures it partially dissociates into CO and O_2, i.e., the interaction of the gas−in which the decomposition is carried out−with the test material differs in the cases considered. Consequently, the gas in which the decomposition is carried out does not play a decisive role when determinations are made in a rapid stream. A common feature of all the analytical methods involving a rapid gas stream is that decomposition proceeds at the same rate as in the test tube, which behaves as a semisealed zone, from which the gas stream cannot carry out with it the vapors of the test material and the inactive decomposition products. We should like to emphasize that the time for which the vapor of the test material is in contact with the hot surface of the test tube walls and with the hot gas is determined, not by the fas flow rate, as inevitably occurs during evaporation from a boat, but by the analyst, who by carefully following the decomposition can carry out the process at faster or slower rates depending on the properties of the test compound.

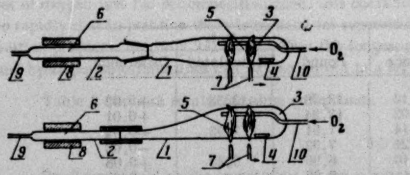


Fig. 1. Tube for highspeed combustion with a ground joint (above) and rubber fitting (below). 1) First part of the tube from the test tube l = 130 mm, d = 15-17 mm; 2) second part of the tube l = 160 mm, d = 5 mm; 3) outlet (l = 80 mm, d = 2 mm), along which the oxygen passes; 4) sample aliquot; 5) decomposition zone; 6) oxidation zone; 7) burner; 8) oven (l = 110 mm) at 950°; 9) end of tube to which the absorption apparatus is connected; 10) outlet (l = 60 mm, d = 2 mm) which is connected to the oxygen supply system.

Complete thermal decomposition can be regarded as a three stage process:

1. Decomposition of the material in the solid or liquid phase with formation of gaseous products, during which the compound either preserves its structure, or the molecule breaks down with formation of fragments with low activity.

2. Decomposition of the material in the gaseous phase with formation of active fragments.

3. Oxidation, hydrogenation, or some other destructive breakdown of the active molecules; this last process always proceeds very rapidly.

Decomposition of the test material in the solid or liquid phase is a direct function of the heating rate, which is controlled by the analyst so that the decomposition only occurs inside the semisealed zone. Since the dimensions of the test tube do not guarantee decomposition of the whole mass of sample all at once, the process must be carried out gradually, and its rate limited by the capacity of the test tube. The rate can only be increased in those cases where the volume of the semisealed decomposition is increased. Subsequent decomposition of test material depends not so much on the rate of heating as on the temperature. In a large semisealed zone the active fragments of the compound can react further. This last process occurs so rapidly in oxygen that it is almost complete inside the decomposition zone and it is the final combustion products that pass almost completely into the oxidation zone.

On the basis of what has been said above, we have developed a rapid and simple method for carbon and hydrogen determination. In this design we retained the semisealed zone, but increased its size so that combustion could be carried out as fast as possible. Since the test tube had been increased in size, that of the combustion tube could not be increased, since an increase in the size of the latter would affect the purging time; its design, therefore, had to be modified. By connecting the test tube, in which decomposition was carried out with the combustion tube into one unit (Fig. 1), we were able to increase the decomposition zone appreciably and at the same time only alter the total volume of the combustion tube to a small extent. As we established, combustion can be carried out very rapidly (in 2-3 min) in such an apparatus, without need for control on the part of the analyst.

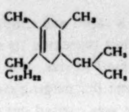
The principle of the highspeed combustion method we have developed consists in rapid combustion of test material in a large semisealed decomposition zone in a rapid stream of oxygen. Oxidation products are absorbed and determined as usual. The method has also proved suitable for analyzing compounds with angular methyl groups; such compounds are known to be the most difficult to analyze.

EXPERIMENTAL

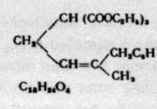
Experimental Procedure. Analysis is carried out in the usual apparatus used for rapid determination of carbon and hydrogen. The combustion tube is made from transparent quartz and consists of two parts connected together either via a ground joint (Fig. 1) or joint to joint covered with rubber. (Fig. 1). The oxygen passes into the first part of the tube through an 80 mm long quartz capillary fused internally and bent toward the wall. This capillary is a continuation of the outlet which connects the tube with the oxygen purifying system. The tube itself is wider than the usual tubes and is constricted toward the point at which it is connected to the second part. The second part of the tube is straight, is 200-280 mm long and has an internal diameter of 7 mm. The end of the tube is drawn out as usual and is connected to the absorption apparatus. A 3-10 mg aliquot contained in a boat or in a quartz capillary is placed in the sealed end of the tube, which acts as a semisealed decomposition zone (the open end of the capillary containing an aliquot should reach the bottom of the tube). An electric oven 70-110 mm long (oxidation zone) heated to 950° is fitted on the second part of the tube. Both parts of the tube are connected and combustion commenced. Combustion is carried out with two burners. One (the stationary one) burner is fixed at the point at which the oxygen enters the apparatus, while the second (the movable one) burner is moved away from the first toward the sealed end of the tube. The material flashes and burns. Combustion takes 2-3 min. Very rarely, only in the case of materials

Table 2

Test material	C, %			H, %		
	Found	Calculated	Difference	Found	Calculated	Difference
I	86,50	86,66	0,16	13,36	13,33	+0,03
	86,64		−0,02	13,34		+0,01
II	71,16	71,02	+0,14	7,91	7,95	−0,04
	71,23		+0,21	7,93		−0,02
III	78,13	78,23	−0,10	6,96	6,88	+0,08
	78,12		−0,11	6,90		−0,02
IV	59,85	59,57	+0,28	6,57	6,43	+0,15
	59,87		+0,30	6,54		+0,11
V	58,05	58,17	−0,12	5,78	5,49	−0,29
	58,06		−0,11	5,76		−0,27
VI	52,56	52,74	−0,18	5,55	5,53	+0,02
	52,60		−0,14	5,63		+0,10
VII	77,93	78,01	−0,08	9,08	9,00	+0,08
	78,13		+0,12	9,13		+0,13
VIII	70,96	71,02	−0,06	7,94	7,95	−0,01
	70,94		−0,08	7,86		−0,09
IX	84,92	84,87	+0,05	14,92	15,13	−0,21
	84,98		+0,11	15,00		−0,13
X	65,86	65,91	−0,05	7,74	7,74	0,00
	65,87		−0,04	7,82		+0,08
XI	57,12	57,13	−0,01	6,07	6,16	−0,09
	57,10		+0,05	6,26		+0,10
XII	93,72	93,68	+0,04	6,32	6,32	0,00
	93,60		−0,08	6,42		+0,10


CH₃
CH₃
CH₃
CH
CH₃
CH₃
$C_{13}H_{24}$

I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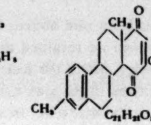
CH₃
CH=C
CH₂C₆H₅
CH₃
$C_{18}H_{24}O_4$

II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CH₃
CH₃
O
CH₃
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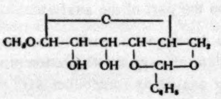
III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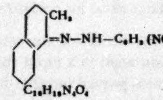
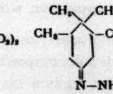
OH OH O—CH—O
C₆H₅

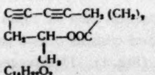
IV


CH₃
=N—NH—C₆H₃ (NO₂)₂
$C_{16}H_{14}N_4O_4$

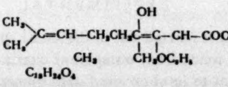
V


CH₃ CH₃
CH₃
COOH
N—NHC₆H₃ (NO₂)₂
$C_{16}H_{20}O_6N_4$

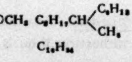
VI


C≡C—C≡C—CH₂ (CH₂)₇
CH₂—CH—OOC
CH₃
$C_{16}H_{22}O_2$

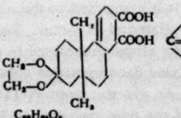
VII


OH
CH₃
CH₃
C=CH—CH₂CH₂C=C—CH—COOCH₃
CH₃
CH₂OC₆H₅
$C_{18}H_{24}O_4$

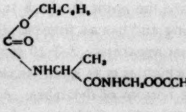
VIII


C₈H₁₇CH
C₆H₁₃
CH₃
$C_{16}H_{34}$

IX


CH₃
COOH
COOH
CH₂—O
CH₂—O
CH₃
$C_{20}H_{20}O_6$

X


CH₂C₆H₅
O
C=O
NHCH
CH₃
CONHCH₂OOCCH₃

XI

Naphthalene

$C_{10}H_8$

XII

which are difficult to burn, is it necessary after 2 min to move the burner away for 1-2 min in order to let in a fresh lot of oxygen into the decomposition zone; this operation is repeated after heating for 2-3 min. Combustion proceeds so rapidly that in practice there is no need for supervision. 250-300 ml of oxygen is used for clearing out the combustion products, i.e.,only 7-10 min. Thus the longest part of the analysis is the weighing operation. Twelve carbon and hydrogen determinations can be carried out in a six-hour working day.

Table 2 contains results for some compounds.

SUMMARY

Emphasis is laid on the importance of the semisealed decomposition zone for quantitative decomposition of organic compounds in a gas stream. It has been shown that the time required for complete decomposition of a sample of test material is shorter, the larger the size of the decomposition zone. A new method for the combustion of organic compounds has been developed for the microdetermination of C and H. When this technique is used decomposition in a large semisealed zone is complete within 2-3 min and does not require supervision on the part of the analyst. The accuracy of the method is ± 0.3%.

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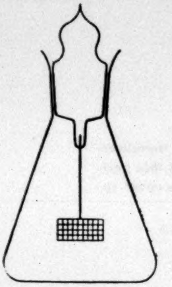
A RAPID MICROMETHOD FOR THE DETERMINATION OF FLUORINE IN MONOMERIC AND POLYMERIC FLUOROORGANIC COMPOUNDS

A. I. Lebedeva, N. A. Nikolaeva, and V. A. Orestova
Institute of High Molecular Weight Compounds, Academy of Sciences,
USSR, Leningrad
pp. 469-471, July - August 1961
Original Article submitted September 12, 1960

Various micromethods have been published for the determination of fluroine in fluoroorganic compounds [1-15]. Schoniger's simple and rapid method [16] suited our purpose best. We carried out combustion of fluoroorganic compounds in a closed flask filled with oxygen (diagram), the gaseous products formed being absorbed with twice-distilled water. Instead of titrating with cerium chloride in the presence of murexide, we determined fluoride ions by direct titration with thorium nitrate, using sodium alizarinsulfonate as indicator. The normality of the Th $(NO_3)_4$ was determined by means of pure fluoracetamide; this technique eliminates the necessity of applying a correction during determination of the fluorine content (only a blank test is carried out). The titration is carried out in the same flask as that used for combustion. The results given in Table 1 show that the error does not exceed ±0.3%.



Combustion flask.

The percentage content of fluorine in polymeric compounds was determined by two methods.

1. By the method suggested by Gel'man et al [14] for the simultaneous determination of carbon, hydrogen, and fluorine, in which the magnesium fluoride is subsequently pyrohydrolyzed and a calibration curve is used; all the corrections recommended by the author were applied.

2. By the method suggested above, which does not involve the use of a calibration curve, and only a blank is taken into account.

For fluorine contents less than 60% the solution being titrated was diluted with water to a constant volume of 50 ml; for higher fluorine contents the volume was made up to 100 ml. 3-7 mg aliquots were used.

In the case of high fluorine contents, and in the absence of hydrogen in the fluoroorganic compound, a small amount of pure paraffin (about 3-5 mg) was added to the test aliquot before combusion in order to ensure complete decomposition. 12-16 determinations can be carried out in a 6 hr working day.

Determination of Fluorine. An aliquot of fluoroorganic compound (3-7 mg) was wrapped up in filter paper and ignited in a platinum grid in a 250 ml flask with a standard ground joint (see diagram). Ten ml of twice-distilled water had been introduced into the flask beforehand. The contents of the flask were shaken for 3-5 min until the vapour cloud had disappeared. The experimental technique has been described earlier [17]. The flask was opened and the volume of liquid made up to 50 ml. 0.6 ml of 1% alizarin red S was added. The solution was neutralized with 0.1 N NaOH until the solution had a red color; 1-2 drops of 0.025 N HNO_3 was then added until a yellow colored developed. In order to establish the requisite pH (2.9-3.00) 3.5 ml of buffer mixture (1 N $CH_2ClCOOH$ + 1 N NaOH; 1:1) was added. The whole sample was titrated in the same flask with 0.025 N Th $(NO_3)_4$. The volume of Th $(NO_3)_4$ used up for titrating the blank (about 0.04 ml) was subtracted from the volume of titrant used for titrating the sample. The blank was carried out under the same conditions but without a sample.

The normality of the Th $(NO_3)_4$ solution was established by means of aliquots (3-5 mg) of pure fluoroacetamide dried to constant weight at 55-60°.

Table 1

Test Material	Sample wt, mg	Fluorine content %: Found	Fluorine content %: Cal.	Difference
Fluoroacetamide C_2H_4FNO	3,670 3,925	24,57 24,54	24,66	−0,09 −0,12
Benzotrifluoride $C_7H_5F_3$	2,595 3,220	38,99 38,88	39,01	−0,02 −0,13
Mono-ß-trifluoroethylamidemaleic acid*. $C_6H_6F_3NO_3$	5,155 5,915	28,62 28,81	28,92	−0,30 −0,11
Mono-ß-trifluoroethylamidecitraconic acid* $C_7H_8F_3NO_3$	2,875 3,000	26,74 27,00	27,00	−0,26 ±0,00
ψ-Fluoroamylmethacryclate of $C_9H_8F_8O_2$	4,107 6,258	50,74 50,72	50,64	+0,10 +0,08
2,4-Dinitrophenylhydrazone-1,1,1-trifluoroacetone $C_9H_7F_3N_4O_4$	5,675 7,320	19,21 19,33	19,50	−0,29
Trifluoromethylphenylmethacrylamide $C_{11}H_{10}F_3NO$	2,660 2,710	24,87 24,95	24,87	−0,17 ±0,00
Tenoyltrifluoroacetone $C_8H_5F_3O_2S$	6,185 4,995	25,53 25,44	25,65	+0,08 −0,12 −0,21
Mixture of fluoroacetamide and tetrachlorophthalic anhydride $C_2H_4FNO + C_8Cl_4O_3$	2,840 +4,110 +3,410 3,715	24,82 24,90	24,66	+0,16 0,24
Mixture of fluoroacetamide and thiocyanochloro $C_2H_4FNO + C_7H_4ClNS$	3,350 +3,680	24,60	24,66	−0,06
Mixture of tenoyltrifluoroacetone and tetrachlorophthalic anhydride $C_8H_5F_3O_2S + C_8Cl_4O_3$	3,795 +3,860 4,580 +3,365	25,38 25,47	25,65	−0,27 −0,18

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* These samples were synthesized by T. V. Sheremetova, Z. V. Borisova, and V. V. Kudryavtsev.

Table 2

Test Material	F found, %: By pyrohydrolysis with MgO	F found, %: By combustion in a flask
Polytetrafluorethylene $(-C_2F_4^-)^n$	75.98*	76.08 75.74
Polymer 1**	8.83 8.77	8.87 9.09
Polymer 2	10.61	10.48 10.33
Polymer 3	19.73 19.74	19.61 19.83
Polymer 4	33.38 33.26	33.21 33.30

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* The theoretical fluorine content is given for Teflon

** These polymers were synthesized at the Institute of High Molecular Weight Compounds, Academy of Sciences, USSR.

SUMMARY

A rapid micromethod is suggested for the determination of fluorine in monomeric and polymeric fluoroorganic compounds. The determination is carried out by combustion of an aliquot of test material in a flask filled with oxygen, followed by absorption of the combustion products with twice-distilled water, and titration of hydrofluoric acid with 0.025 N $Th(NO_3)_4$, using alizarin red S.

A small amount of pure paraffin (3-5 mg) is added to fluoroorganic compounds which do not contain hydrogen in order to ensure their complete decomposition.

The method is rapid, the apparatus is simple, and there is no need to transfer the absorption liquid into another vessel. Nitrogen, sulfur, and chlorine do not interfere with the determination. The experimental error is ± 0.3%. One determination takes 20-25 min.

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SIMULTANEOUS DETERMINATION OF FLUORINE, SILICON, AND CHLORINE IN SILICOORGANIC COMPOUNDS CONTAINING FLOURINE AND CHLORINE

E. A. Bendarevskaya, V. M. Kuznetsova, and S. V. Syavtsillo

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 4,
pp 472-476, July-August, 1961
Original Article submitted June 14, 1960

Series of articles are being published at present on the development of methods for the determination of fluorine [1-7], the simultaneous determination of carbon and fluorine [8,9], simultaneous determination of carbon, hydrogen, and fluorine [10-15], fluorine and nitrogen [16], and silicon [17] in compounds of the type $H(CF_2CF_2)_x SiCl_3$. There are no published methods on the simultaneous determination of silicon, chlorine, and fluorine in fluorochlorosilicoorganic compounds.

Table 1

Test Material	Sample wt.,mg	Found %		Deviation from the theoretical value %	
		F	Si	F	Si
$(CF_3CH_2CH_2)_2Si(OC_3H_7)_2$*	25,684	39,7	7,5	—0,9	—0,4
Calculated 40,6% F; 7,9% Si	20,901	39,9	7,8	—0,7	—0,1
$CF_3CH_2CH_2(CH_3)Si(OC_2H_5)_2$*	35,433	24,5	12,6	—0,3	+0,4
Calculated 24,8% F; 12,2% Si	20,001	24,9	12,1	+0,1	—0,1
$F_2C_6H_3(CH_3)Si(OC_2H_5)_2$	15,018	15,9	11,6	+0,5	+0,2
Calculated 15,4% F; 11,4% Si	18,990	15,1	11,9	—0,3	+0,5
$FC_6H_4(CH_3)Si(OC_2H_5)_2$	31,221	8,2	12,8	—0,1	+0,5
Calculated 8,3% F; 12,3% Si	18,426	7,9	12,5	—0,4	+0,2

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* A.L. Klebanskii prepared the pure materials which he kindly gave us to develop the method.

Table 2

Test Material	Sample wt.,mg	Found %		Deviation from the theoretical value,%	
		F	Si	F	Si
Polymer № 1	44,310	23,0	20,9	+0,4	+0,1
Calculated 22,6% F; 20,8% Si	50,080	22,8	21,4	+0,2	+0,5
Polymer № 2	40,349	35,9	17,7	+0,5	—0,2
Calculated 36,5% F; 17,9% Si	56,384	36,7	17,4	+0,2	—0,5
Polymer № 3	28,911	22,2	14,8	+0,4	+0,5
Calculated 21,8% F; 14,3% Si	47,876	22,4	14,7	+0,6	+0,4

During a study of a method for determining fluorine in organic compounds [1] which is applicable to fluorine-containing silicoorganic materials, we established that it is possible to determine fluorine, chlorine, and silicon simultaneously.

Essentially, the cited method of determining fluorine [1] consists in fusing an aliquot of the fluoroorganic compound with potassium metal in a steel bomb at 800-850° for 10-15 min. The melt obtained is dissolved in water, and fluoride is determined in an aliquot of the solution by titration with thorium nitrate. The authors have examined the possibility of determining fluorine in the presence of chlorine, sulfur, nitrogen, and phosphorus.

Table 3

Test Material	Sample wt.,mg	Decomposed for 45 min at 950°		Decomposed for one hour at 1000°	
		F	Si	F	Si
$(CH_3)(C_6H_3F_2)_2SiCl$	30,355	18,1	9,7		
	32,046	19,4	10,0		
Calculated 25,0% F; 9,5% Si	31,848			17,5	10,2
	29,001			18,8	9,9
Polymer № 4	38,222	16,4	14,8		
	40,081	16,0	14,6		
Calculated 23,0% F; 14,6% Si	25,016			17,0	14,7
	39,495			16,6	14,9

Table 4

Test Material	Sample wt.,mg	Decomp. in oxygen atmosphere			
		45 min 1000°		60 min 1000°	
		F	Si	F	Si
$(CH_3)(C_6H_3F_2)_2SiCl$	39,392	19,2	10,1		
	37,455	19,9	10,1		
Calculated 25,0% F; 9,5% Si	41,040			25,4	10,1
	23,000			25,4	9,8
Polymer № 4	27,961	16,8	14,7		
	29,351	16,5	14,4		
Calculated 23,0% F; 14,6% Si	28,931			23,3	14,5
	32,466			22,9	14,7
$(F_2C_6H_3)_2(CH_3)Si(OC_2H_5)$	28,606			24,7	8,3
Calculated 24,2% F; 8,9% Si	20,333			24,1	8,0

Silicon can be determined titrimetrically by the hydroxyquinoline and acidimetric methods. The first method, which is based on formation of a sparingly soluble silicomolybdate hydroxyquinoline complex [18-20], has not found wide application. Stobba [21] was the first to suggest the acidimetric method, and it was subsequently improved and modified by many workers [22-27]. The simplest and most reliable variant of this method is based on formation of ammonium silicofluorosilicate in the presence of hydrochloric acid. The silicon content is determined from the amount of hydrochloric acid which participates in the reaction, i.e., the determination reduces to titration of excess acid with alkali [27]. $Si(OH)_4 + 6NH_4F + 4HCl = (NH_4)_2SIF_6 + 4H_4Cl + 4H2O$. In order to avoid side reactions of fluorine with glass, and also of glass with alkali, we used gelatin capsules or polyethylene ampoules for holding the samples. We made the latter from polyethylene tubing of suitable diameter.

The method was developed using individual monomeric silicofluoroorganic compounds, whose carbon and hydrogen contents, refractive index, specific gravity, and molecular refraction corresponded to those of the chemically pure materials *.

The experimental results obtained showed that the time required to decompose some silicoorganic compounds containing fluorine is 45 min at 900-950°. The color change at the end point was not clearly defined on titrating with 0.01 N KOH, and variable results were obtained for silicon, mainly results on the low side. Accordingly, in our subsequent experiments we determined silicon by titrating the acid with 0.1 N alkali solution.

Table 1 contains the results obtained during simultaneous determination of F and Si in individual monomeric silicofluoroorganic compounds containing one or two fluorine atoms on one phenyl or alkyl radical.

Analysis of pure polymeric silicoorganic compounds containing fluorine in the aliphatic radicals showed that it should be possible to determine fluorine and silicon simultaneously in these compounds with reasonable accuracy (Table 2).

---

* K.P. Grinevich made the chemically pure materials, which he kindly gave us to develop the method.

Table 5

Test Material	Sample wt. mg	Found %			Deviation from the theoretical value %		
		F	Si	Cl	F	Si	Cl
$(C_2H_5)(CH_3)(C_6H_3F_2)SiCl$	26,843	16,9	12,6	15,7	—0,2	0	—0,4
Calculated 17,1% F; 12,6% Si; 16,1% Cl	27,498	17,0	12,6	15,9	—0,1	0	—0,2
$(F_2C_6H_3)(CH_3)SiCl_2$	42,659	17,5	13,2	30,9	+0,5	+0,6	0
Calculated 17,0% F; 12,5% Si; 30,9% Cl	26,688	17,4	12,9	30,8	+0,4	+0,4	—0,1
$(C_6H_4F)(CH_3)SiCl_2$	19,173	9,5	13,5	34,1	+0,4	—0,1	+0,1
Calculated 9,1% F; 13,6% Si; 34,0% Cl	12,286	9,2	13,2	33,9	+0,1	—0,4	—0,1
$(CF_3CH_2CH_2)_2SiCl_2$	35,117	39,2	8,9	24,2	+0,3	—0,1	0
Calculated 38,9% F; 9,0% Si; 24,2% Cl	35,712	39,0	8,7	24,4	+0,1	—0,3	+0,2

During analysis of monomeric compounds containing two fluorinated phenyl radicals on the silicon atom, and also during analysis of polymeric compounds with fluorinated phenyl radicals, it was observed that the radicals were split off and that they were incompletely decomposed; accordingly, the silicon was determined quantitatively, while the fluorine was not completely determined (Table 3).

These results can be explained by the values of the energy of the chemical bonds C – F, and C – Si [28]. In the first instance the energy is 104 kcal/mole, while in the second instance it is only 58 kcal/mole.

By fusing test material with potassium metal in an oxygen filled bomb for 60 min at 1000° we were able to destroy the fluorinated radicals completely. It is obvious that not only reducing but also, to some extent, oxidizing reactions occur during this process.

Results of the determination of fluorine and silicon contents are given in Table 4. Chlorine can be determined at the same time as fluorine and silicon, a thiocyanate titration being used for this purpose (Table 5).

Experimental Procedure. A 20-40 mg aliquot of test material contained in polyethylene ampoules or gelatin capsules is placed in a metal bomb, and fused with 4-5 times its amount of potassium metal. The fusion time and the temperature chosen depend on the nature of the test material. When the test material contains one fluorinated phenyl radical or fluorinated alkyl radicals on the silicon atom, fusion is carried out at 900-950° for 40-45 min. When two or more fluorinated phenyl radicals are present on the silicon atom, fusion time is increased to 60 min, and the temperature increased to 1000°. In the latter instance the bomb is swept with oxygen for 2-3 min before an analysis. After fusion, and after the bomb has been cooled, the latter is opened and excess potassium metal carefully removed by addition of water; the contents of the bomb are then quantitatively transferred to a 200 ml standard flask. Fluorine, chlorine, and silicon are then determined by separate titration of aliquots of this solution.

Fluorine is determined by the method described in [1]. Chlorine is determined by a thiocyanate titration [29].

Silicon Determination. Twenty-five ml of the solution is transferred to a titration flask, 5-6 drops of indicator* is added, and the solution neutralized first with HCl (1:1) and (1:10) until it has a weakly acid reaction, and then neutralized accurately with 0.1 N alkali. During this stage the total volume of solution should not exceed 50 ml. The solution is next saturated with potassium chloride (30-50 mg), and again accurately neutralized with 0.1 N alkali solution and 0.1 N acid 2 ml of a neutral solution of ammonium fluoride** is added followed by 10 ml of 0.1 N hydrochloric acid, and excess acid titrated rapidly with alkali. The color change at the end point is from red to green. The silicon content is calculated by means of the formula:

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*The indicator is prepared by mixing the following two solutions: a) 0.1% alcoholic solution of methyl red; b) to 100 ml of an aqueous solution of bromocresol green is added 0.5 ml of 0.1 N NaOH. Six parts of solution(a) is mixed with five parts of solution(b).

**40 ml of 25% ammonia is mixed with 25 ml of 40% hydrofluoric acid. This mixture is then diluted to one liter with water, and after a rough neutralization, neutralized accurately using an indicator. The acidity of the solution prepared is checked daily before use. For this purpose 20 ml of 0.1 N HCl and 10 ml of NH_4F are titrated with 0.1 N KOH. If the amount of alkali differs from the amount of the latter used in titrating the pure acid, then the fluroide solution should be neutralized again.

$$\mathrm{Si}\,\% = \frac{(V - V_0)\,K \cdot 0{,}7015 \cdot 8 \cdot 100}{a},$$

where V is the volume of 0.1 N alkali used in titrating 20 ml of 0.1 N hydrochloric acid [*], ml; V_0 is the volume of 0.1 N alkali[*] used in titrating the acid which has not racted during formation of ammonium silicofluoride, ml; K is the correction for the normality of the 0.1 N alkali; 0.7015 is the amount in mg of silicon corresponding to 1 ml of 0.1 N hydrochloric acid; a is the sample weight; 8 is the dilution factor.

SUMMARY

A method is suggested for the simultaneous determination of fluorine, silicon, and chlorine in some monomeric and polymeric silicoorganic compounds containing fluorine and chlorine. The accuracy of the method is 0.2-0.5% absolute.

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[*] The 0.1 N HCl is standardized against potassium iodate using a mixed indicator. The 0.1 N KOH is standardized against the 0.1 N HCl using the same indicator.

POLAROGRAPHIC DETERMINATION OF 2-METHYL-5-VINYLPYRIDINE

V.D. Bezuglyi, V.N. Dmitrieva, T.A. Alekseeva, and G.G. Belous

All-Union Scientific-Research Institute of Monocrystals and Highly Pure Materials, Khar'kov

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In recent years 2-methyl-5-vinylpyridine has acquired importance as a monomer in the production of synthetic rubbers, and also of various copolymers, including, e.g., copolymers with acrylonitrile and methylmethacrylate (U.S.A. Patent 2688012, Ref. Zh. Khim. 1956, No. 41293) etc. Copolymerization of 2-methyl-5-vinylpyridine with styrene may also be of special importance in certain specific cases. The necessity of determining this monomer quantitatively, particularly during a study of its polymerization (or copolymerization) kinetics, makes it essential to find methods which will enable changes in the amount of this compound in reaction mixtures and also in polymers to be determined rapidly and objectively.

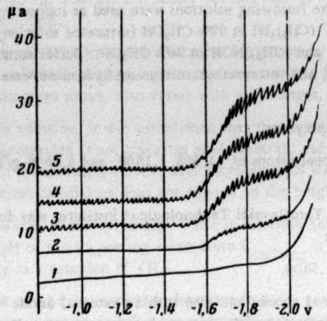


Fig. 1. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a saturated solution of $(CH_3)_4NI$ in 92% CH_3OH against an internal anode (E = − 0.413 v). 1) Supporting electrolyte; 2) 0.034 g/liter; 3) 0.096 g/liter; 4) 0.124 g/liter; 5) 0.151 g/liter.

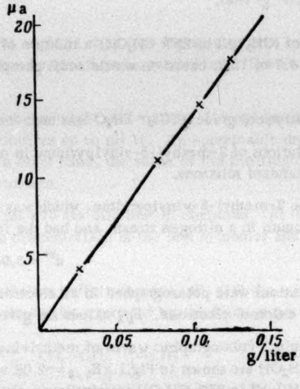


Fig. 2. Calibration curve for methylvinylpyridine in a supporting electrolyte of $(CH_3)_4NI$ in 92% CH_3OH.

The authors' experience in recent years has convinced them that the polarographic method is of definite importance for solving such problems. Although a considerable number of papers have been published which have been devoted to polarographic studies of pyridine and some of its derivatives [1-5], we have not seen any published information on the polarographic behavior of methylvinylpyridine.

In this connection we have carried out a detailed study of the polarographic activity of this compound, and on the basis of the results obtained we have developed methods for its qualitative polarographic determination.

Experimental Procedure. Polarographic measurements were made on a photorecording M-103 polarograph, using a dropping mercury electrode with the following characteristics: m = 2.354 mg/sec, τ = 3.5 sec. (at E = O). In some instances we also used a Sommer type capillary [6] with τ from 3 to 1.5 sec; nevertheless we cannot recommend this type, because its dropping period is not stable enough.

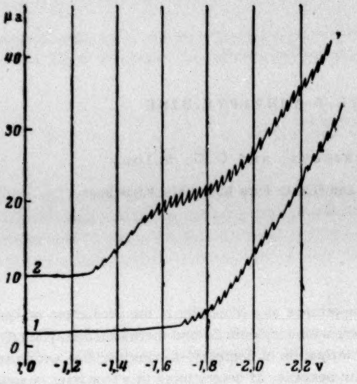


Fig. 3. Polarographic wave for methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 5.85. 1) Supporting electrolyte; 2) 0.307 g/liter.

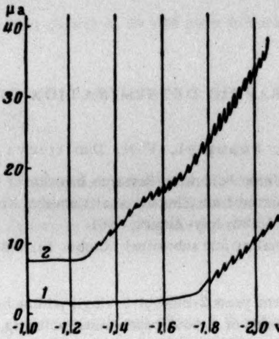


Fig. 4. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 6.45. 1) Supporting electrolyte; 2) 0.079 g/liter.

The following solutions were used as supporting electrolytes: $(CH_3)_4NI$ in 92% CH_3OH (saturated solution); 0.05 N solution of $(CH_3)_4NI$ in 25% CH_3OH; a mixture of 0.05 N $(CH_3)_4NCl$ and $(CH_3)_4NOH$ in 20% CH_3OH. Buffer solutions with pH from 4.7 to 12.2, based on acetic acid, phosphoric acid, phenol, and tetramethylammonium hydroxide were also used.

Analytical grade $AlCl_3 \cdot 6H_2O$ was used for precipitating the polymer.

Solutions of 2-methyl-5-vinylpyridine in methanol with concentrations of 11.508, 1.1508, and 2.2576 g/liter were used as standard solutions.

The 2-methyl-5-vinylpyridine, which was synthesized at the Yaroslavskii Technological Institute, was distilled under vacuum in a nitrogen stream and had the following constants:

$$d^{25} = 0.9564 \text{ g/cm}^3;\ n_D^{20} = 1.5430.$$

Solutions were polarographed in an electrolyzer with an internal anode, and also with an external anode – a saturated calomel electrode. $E_{1/2}$ values are given relative to the potential of the saturated calomel electrode.

Results. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a saturated solution of $(CH_3)_4NI$ in 92% CH_3OH are shown in Fig. 1. $E_{1/2} = -2.08$ v. Waves of methylvinylpyridine in a supporting electrolyte of 0.05 N $(CH_3)_4NI$ in 25% CH_3OH are similar in character; $E_{1/2} = -2.04$ v.

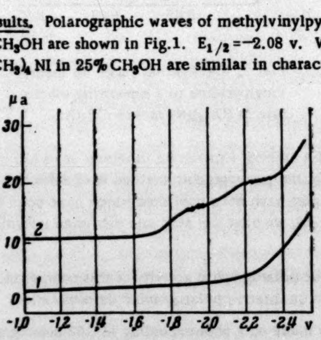


Fig. 5. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 9.74. 1) Supporting electrolyte; 2) 0.152 g/liter.

TABLE 1. Diffusion Current Constants for Methylvinylpyridine in a Supporting Electrolyte of $(CH_3)_4NI$ in 92% CH_3OH

c, mM/liter	I_d, μa	$K = \frac{I_d}{m^{2/3}\tau^{1/6}c}$
0,285	2,80	5,24
0,807	7,865	5,09
1,045	10,368	5,18
1,269	12,513	5,15

TABLE 2. Determination of Methylvinylpyridine in Synthetic Mixtures

Monomer in the polymer, %		Error (relative), %
Taken	Found	
2.78	2.68	−3.6
3.33	3.40	+2.1
11.31	11.40	+0.64
12.24	12.80	+4.6
13.14	13.08	−0.61
14.09	14.16	+0.66

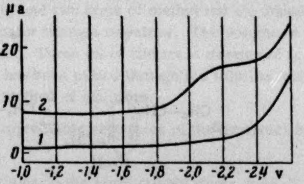


Fig. 6. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 11.65. 1) Supporting electrolyte; 2) 0.153 g/liter.

The value of the diffusion current of methylvinylpyridine is a linear function of its concentration (Fig. 2); this is also confirmed by the constancy of the diffusion current constant at different concentrations of the test material (Table 1).

During a study of the effect of pH on the polarographic indices of 2-methyl-5-vinylpyridine, the results shown in Figs. 3, 4, 5, and 6 were obtained. In the course of this work it was established that one wave with a poorly defined limiting current zone is observed in acid solutions, so that the wave height cannot be measured sufficiently accurately.

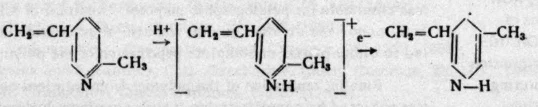
Starting from pH 6 a poorly defined second wave appears which almost coincides with the wave for the supporting electrolyte.

At pH 9.74 both waves become fairly clearly distinguishable, but at pH 11 they fuse together to give one wave with a well defined limiting current zone suitable for polarographic measurements to be carried out. The wave height, as the diagram shows, also varies with pH changes.

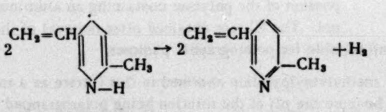
In addition, it was established that the relationship between the wave height of 2-methyl-5-vinylpyridine and its concentration is not linear in acid, neutral, and weakly alkaline solutions up to pH 10. An appreciable drop in the value of the limiting current with increasing pH was observed. On the other hand, the value of the limiting current under these conditions does not depend on the height of the mercury column.

Waves of methylvinylpyridine in alkaline buffer solutions with pH ≥10 are different in character. At these values of the pH of the supporting electrolyte I_{limiting} is proportional to the concentration of the test monomer and changes linearly as a function of $\sqrt{H}$.

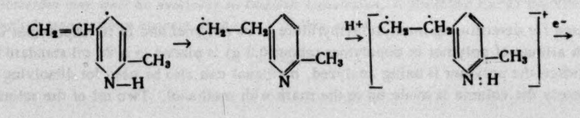
It can be assumed therefore that in acid, neutral, and weakly alkaline buffer solutions (pH <10) the waves are catalytic in nature and that the electrode process corresponding to them can be expressed by the following scheme:

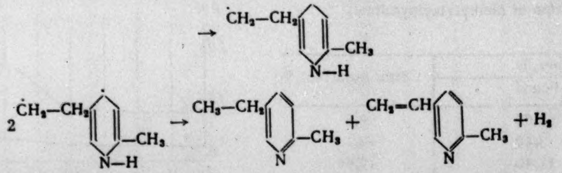


In acid buffer solutions

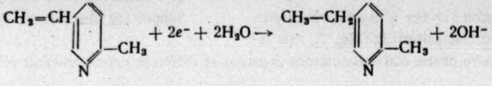


In neutral and weakly alkaline buffer solutions





In alkaline solutions with pH>10 reduction of 2-methyl-5-vinylpyridine is diffusive in character and is expressed by the following scheme:



Quantitative Determination of 2-Methyl-5-Vinylpyridine. Quantitative determination of 2-methyl-5-vinylpyridine in pure solutions does not present any difficulties and can be readily carried out in supporting electrolytes of buffer solutions with pH from 11 upward, both by using a calibration curve, and by the method of additions. It is considerably more difficult to determine this monomer in polymethylvinylpyridine, and also in its copolymer with styrene.

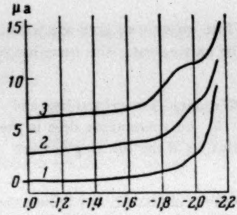


Fig. 7. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a mixture of $(CH_3)_4$ NCl and $(CH_3)_4$ NOH for various concentrations of $(CH_3)_4$ NOH in 20% CH_3OH (filtrate obtained after precipitation of the polymer). 1) Supporting electrolyte; 2) 0.072 g/liter; 3) 0.072 g/liter + 0.011 M $(CH_3)_4NOH$.

In addition to being soluble in such solvents as benzene, dioxane, and chlorinated hydrocarbons, methylvinylpyridine is also soluble in alcohols. Methanol cannot therefore be used as a precipitant for these polymers in the given instance.

When polarograms were taken of methylvinylpyridine in the presence of the polymer in a supporting electrolyte of $(CH_3)_4NI$ in 92% CH_3OH, a distorted wave was obtained for methylvinylpyridine, with a maximum which fused with the reduction wave of the supporting electrolyte, while the galvanometer needle oscillated violently.

In 1:4 and 1:5 methanol-water mixtures, polymethylvinylpyridine gives a stable suspension, the particles of which carry a positive charge. Salting out of the polymer proved to be a very difficult problem. Centrifuging, and filtering through a fine filter (a layer of Al_2O_3, No. 3 and No. 4 glass filters) only led to partial separation of the polymer. The filtrate obtained under these conditions was unsuitable for polarographic purposes. Addition of solutions of salts with both mono- and divalent anions, and also of acids and alkalis, to the suspension, led to either partial or complete peptization of the polymer.

Finally, separation of the polymer from solutions containing the monomer was achieved by coprecipitating it with aluminum hydroxide, by gradual addition of a solution of tetramethylammonium hydroxide to an aqueous methanol suspension of the polymer containing an aluminum salt in the presence of methyl red. The filtrate obtained after removal of the polymer precipitated with the aluminum hydroxide was clear and suitable for polarographic purposes.

The polarographic wave of methylvinylpyridine obtained in this filtrate as a supporting electrolyte was, however, poorly defined (Fig. 7, Curve 2), because the pH of the solution being polarographed was not high enough. By adding a small amount of $(CH_3)_4NOH$ to the filtrate, a polarographic wave was obtained for methylvinylpyridine which was suitable for measurement (Fig. 7, Curve 3).

The method used for determining methylvinylpyridine in its polymer and in its copolymer with styrene reduces to the following. An aliquot of polymer or copolymer (about 0.3 g) is placed in a 25 ml standard flask and is dissolved in 5 ml of dioxane (when the polymer is being analyzed, methanol can also be used for dissolving it). After the sample has dissolved completely the volume is made up to the mark with methanol. Two ml of the solution obtained is transferred to a 10 ml standard flask, 6 ml of water, 0.3 ml of 1 N $AlCl_3$, and two drops of methyl red are added and 0.4 N $(CH_3)_4NOH$ then added in small portions until the color of the indicator changes to yellow. The volume of the mixture is made up to the mark with water and then filtered into a dry vessel. Three ml of filtrate is transferred to the electrolyzer, 0.2-0.4 ml of 0.4 N $(CH_3)_4NOH$ is added, and after nitrogen has been passed through the solution, polarograms are taken. The methylvinylpyridine content is determined by the method of additions.

It is clear from the results given in Table 2 that there is no appreciable absorption of the monomer by the polymer.

The values obtained during determination of methylvinylpyridine in the same sample were: 2.46, 2.38, 2.56, 2.57, 2.41, 2.59, 2.53, 2.45, 2.54, 2.50 g/liter.

The relative experimental error was determined by statistical treatment of the results obtained, using the formula

$$\varepsilon_{\text{rel.}} = \frac{t_\alpha S}{\bar{x}\sqrt{n}} \cdot 100\%,$$

where $\underline{n}$ is the number of determinations, $\bar{x}$ is the arithmetic mean of $\underline{n}$ determinations, S is the mean square error of an individual determination calculated by the usual formula, $\underline{\alpha}$ is the confidence level (reliability) (in the given instance $\alpha = 0.95$), and t_α is a multiplier dependent on $\underline{n}$ and $\underline{\alpha}$ (see [7]).

The relative error in our case proved to be 2.1%.

The method which we have developed for the quantitative determination of 2-methyl-5-vinylpyridine has been used for studying its polymerization kinetics.

SUMMARY

A study has been made of the polarographic behavior of 2-methyl-5-vinylpyridine in a supporting electrolyte of $(CH_3)_4NI$ in methanol and aqueous methanol solutions, and also in a supporting electrolyte of buffer solutions with different pH values.

A method has been developed for the determination of methylvinylpyridine in its polymers and in its copolymer with styrene. It is based on separation of the polymer from solutions containing the monomer, by coprecipitating the former with $Al(OH)_3$ and taking polarograms of the filtrate in a supporting electrolyte of $(CH_3)_4NOH$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A POLAROGRAPHIC STUDY OF TEREPHTHALIC AND PARA-TOLUIC ACIDS, THEIR NITRO DERIVATIVES, DIMETHYL TEREPHTHALATE, DIMETHYL NITROTEREPHTHALATE, AND METHYL PARATOLUATE

Ya.I. Tur'yan and Yu.A. Vakhrushev

State Scientific-Research and Design Institute of the Nitrogen Industry
and of the Products of Organic Synthesis, Lisichansk Branch, Severodonetsk

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Development of polarographic techniques for the determination of terephthalic acid, paratoluic acid, mononitroterephthalic acid, 3-nitroparatoluic acid, dimethyl terephthalate, methyl toluate, and dimethyl nitroterephthalate is of considerable interest both from the point of view of the polarography of organic compounds, and also for production control of the intermediate products obtained during the synthesis of fibers of the lavsan type. Of these compounds only dimethyl terephthalate has been examined polarographically [1-3]. A study has, however, been made of the polarographic behavior of dimethyl terephthalate, but only over a narrow concentration range,since aqueous solutions were used. No success has been achieved in obtaining the polarographic characteristics of terephthalic acid [1,2].

EXPERIMENTAL*

Polarograms were taken on an "Orion" (Hungarian) electronic polarograph. The cell was thermostatted at 25± 0.2°. A mercury pool was used as anode. The half-wave potentials were measured relative to a saturated calomel electrode by means of a potentiometer. Three capillaries with the following characteristics were used $m^{2/3}t^{1/6}$ $1.31^{2/3}$ (I), 1.16 mg sec. (II), and 0.89 $mg^{2/3}sec^{-1/2}$ (III). The characteristics were established by disconnecting the circuit in 0.1 N KCl. Oxygen was removed by means of nitrogen.

Buffer solutions (pH 2-12) prepared according to Britton-Robinson were used.

Twice distilled methanol was used in a series of experiments.

Terephthalic Acid. This acid was prepared by saponifying pure dimethyl terephthalate: m.p. 141-142°, ester number 103. The terephthalic acid obtained distilled at a temperature >300° [4] and had an acid number of 119.6.

The stock solutions of terephthalic acid were prepared in 0.5 N NaOH,followed by neutralization with H_2SO_4 using phenolphthalein as indicator.

It was established that a polarographic wave for terephthalic acid could be obtained in a supporting electrolyte of a buffer solution with pH 4.1-5.2. In order to get more clearly defined polarographic waves it was necessary to add – by analogy with the conditions used for polarographing phthalic acid [5] – 0.05 M $CaCl_2$ (Fig. 1). At pH <4.0 and pH >5, the diffusion current constant of terephthalic acid decreases, this being particularly the case at pH <4.0 (Fig. 2). Formation of a precipitate of terephthalic acid appears to be the reason for this decrease in the latter instance. Precipitation of $Ca_3(PO_4)_2$ makes it difficult to obtain satisfactory waves at pH>5.

Thus the optimum pH range for analytical purposes is 4.4-4.8. The half-wave potential ($E_{1/2}$) over this range, 1.45-1.51 v,linearly increases with increasing pH.

At pH 4.6 the value of i_D is proportional to C over the range 0.1-5.0 mM/liter; the diffusion current constant i_D = 3.70 ± 0.06 μa/mM/liter (capillary I). The relationship between i_D and C is not linear for terephthalic acid concentrations >5.0 mM/liter.

Paratoluic acid does not give a polarographic wave in this supporting electrolyte and does not interfere with de-

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*Z.V. Zaitseva and M.P. Los' took part in the experimental work.

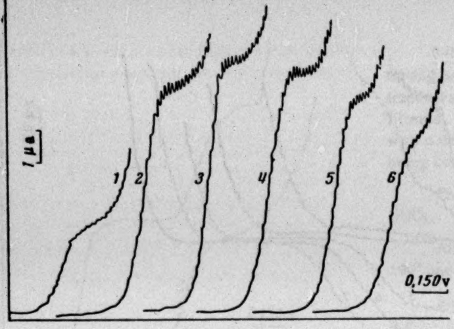

Fig. 1. Polarogram of terephthalic acid at a concentration of 2 × 10^{-3}M. 1) pH 4.1; 2) pH 4.3; 3) pH 4.6; 4) pH 4.7; 5) pH 5.0; 6) pH 5.2. Initial voltage 1.15 v.

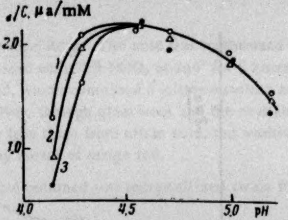

Fig. 2. The relation between the diffusion current constant of terephthalic acid and the pH of the supporting electrolyte. 1) 1.65 × 10^{-3}M; 2) 1.85 × 10^{-3}M; 3) 2.5 × 10^{-3}M.

termination of terephthalic acid.

Nitrate, when present, does not interfere with the polarographic determination of terephthalic acid either.

The polarographic method permits terephthalic acid to be determined in the presence of paratoluic acid and nitric acid. The experimental accuracy, as in the case of the other materials considered below, is not lower than 3-5% (relative).

Paratoluic Acid. This acid was prepared by saponifying methyl paratoluate (m.p. = 32-33°, ester number 66.0). The paratoluic acid has a m.p. of 181-182°, and an acid number of 73.8,

Stock solutions of paratoluic acid were prepared by dissolving the acid in 0.5 N NaOH and then neutralizing.

In a buffering solution, as described above, a polarographic wave for paratoluic acid could not be obtained.

A hydrogen wave with $E_{1/2}$ = 1.57-1.60 v and I_D = 2.6 ± 0.14 µa/mM/liter (capillary III, concentration range 0.1-2 mM/liter) is obtained for solutions of paratoluic acid in a supporting electrolyte of 0.1 N $(CH_3)_4NI$.

In order to determine paratoluic acid we studied the polarographic behavior of its nitration product.

It was established that at low concentrations, paratoluic acid, even at room temperature, is readily nitrated by nitric acid whose concentration in the reaction mixture is not less than 82%. In a solution with a concentration of 0.04 M, paratoluic acid is almost completely nitrated after only five minutes.

A comparison of the polarogram of a solution obtained after nitration (with subsequent neutralization by KOH) with a polarogram of 3-nitroparatoluic acid shows that 3-nitroparatoluic acid is the acid formed during nitration.

The relationship between diffusion current and paratoluic acid concentration over the concentration range 0.01-4.0 mM/liter, at pH 5.0, is linear.

When terephthalic acid solutions are nitrated under the same conditions a polarographic wave is not obtained.

It is possible therefore to determine paratoluic acid polarographically in the presence of excess terephthalic acid.

Nitroterephthalic Acid. Nitroterephthalic acid was prepared by nitrating terephthalic acid with a mixture of 83% HNO_3 and 8% oleum (1:1) at 60° for 40 min. The product obtained was freed from nitric and sulfuric acid with cold water; it was then dissolved in hot water and the solution filtered on a hot filtration funnel.

The nitroterephthalic acid obtained after being recrystallized twice had a m.p. 272-273° and an acid number 94.7 .

In contrast to terephthalic acid, it was not necessary to convert nitroterephthalic acid into a salt in order to dissolve it, since it is itself sufficiently soluble in water.

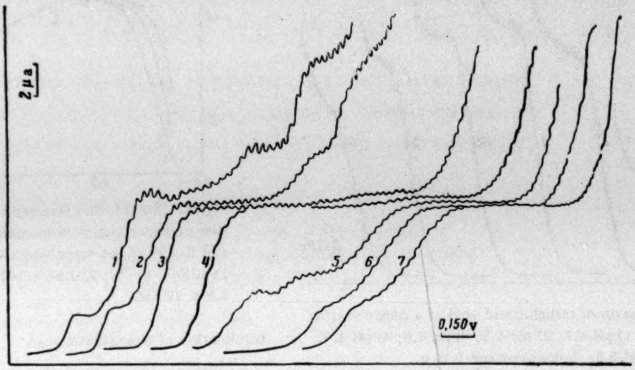

Fig. 3. Polarograms of nitroterephthalic acid at a concentration of 1×10^{-3}M. 1) pH 2.0; 2) pH 4.2; 3) pH 5.0; 4) pH 6.5; 5) pH 8.2; 6) pH 9.2; 7) pH 11.0. Initial voltage 0.04 v.

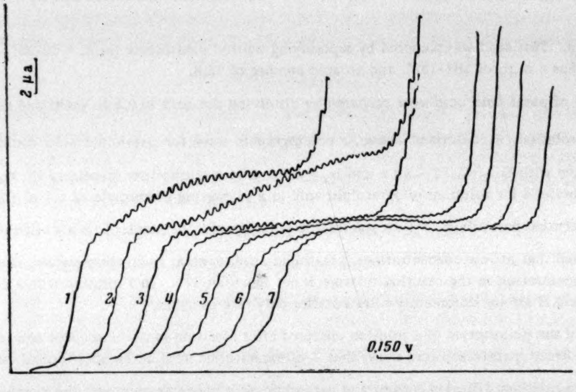

Fig. 4. Polarograms of 3-nitroparatoluic acid at $C = 1 \times 10^{-3}$M. 1) pH 2.2; 2) pH 3.1; 3) pH 4.3; 4) pH 7.4; 5) pH 8.3; 6) pH 9.2; 7) pH 9.7. Initial voltage 0.03 v.

Polarographic waves of nitroterephthalic acid at various pH values of a buffer supporting electrolyte (+0.5 M KCl) are shown in Fig. 3. The nature of the change in the wave with the pH of the supporting electrolyte is similar to that which was observed earlier [6] in the case of nitroterephthalic acids.

It follows from Fig. 3 that the pH range of greatest interest from an analytical point of view is 5.0-6.5, over which one clearly defined polarographic wave is obtained which has a diffusion current constant which is independent of pH, and a half-wave potential $E_{1/2} = 0.36-0.45$ v which increases with increasing pH.

The relation between i_d and C is linear at pH 6.0; the diffusion current constant $I_D = 8.2 \pm 0.1$ μa/mM/liter (capillary I) over the concentration range 0.01-4.0 mM/liter.

Nitroterephthalic acid can be determined polarographically in the presence of a large excess of terephthalic acid; this is very important for production purposes.

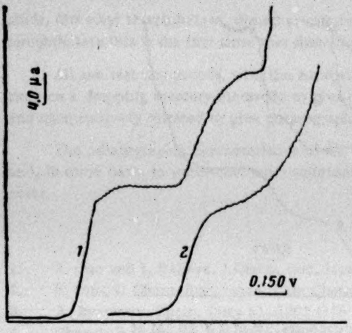

Fig. 5. Polarograms. 1) Dimethyl terephthalate in a supporting electrolyte of 0.05 M $(CH_3)_4NI$ in 80% CH_3OH. Initial voltage 1.2 v; 2) methyl paratoluate in a supporting electrolyte of 0.01 M $(C_2H_5)_4NOH$, 50% CH_3OH. Initial voltage 1.7 v.

3-Nitroparatoluic Acid. The acid was synthesized by nitrating paratoluic acid with 75% HNO_3 at 115° for 6 hours. The suspension obtained, which contained 3-nitroparatoluic acid, was filtered, after cooling, through glass wool and the crystals washed with cold water to free them from nitric acid, the washing process being controlled by means of congo red.

The nitro acid obtained was recrystallized twice from 70% HNO_3.

After purification the product obtained has a m.p. of 189-190° and an acid number of 55.1.

Stock solutions of 3-nitroparatoluic acid were prepared by dissolving the nitro acid in 100% methanol, while polarograms were taken in 20% methanol.

Polarograms of 3-nitroparatoluic acid at various pH values of the buffer supporting electrolyte (+0.5 M KCL) are shown in Fig. 4.

One clearly defined wave whose diffusion current constant is independent of pH is observed at pH 4-8; the half-wave potential $E_{1/2}$ = 0.30-0.65 v, it increases linearly with increasing pH.

The relation between i_d and C is linear. The diffusion current constant is I_D = 7.20 ± 0.04 μa/mM/liter (Capillary I, pH 4.4) over the concentration range 0.01-4.0 mM/liter.

Dimethyl Terephthalate. Commercial dimethyl terephthalate was used (m.p. = 141-142, ester number 103).

Stock solutions were prepared in 100% methanol, while polarograms were taken in 80% CH_3OH in a supporting electrolyte of 0.05 N $(CH_3)_4NI$.

TABLE 1. The Relation between the Limiting Current (i_d) and the Height of the Mercury Reservoir (H)

Test material	Concentration, M	H, cm	i_d, μa	$\frac{i_d}{\sqrt{H}}$, μa·cm$^{-1/2}$
Terephthalic acid	$2\cdot10^{-3}$	33,6	6,48	1,12
		42,0	7,22	1,11
		49.2	7,80	1,11
		58,0	8,62	1,13
Nitroterephthalic acid*	$1\cdot10^{-3}$	34,5	7,50	1,28
		42,0	8,20	1,27
		50,0	9,30	1,30
		58,0	9,90	1,30
3-Nitroparatoluic acid	$5\cdot10^{-4}$	34,5	3,20	0,546
		42,0	3,55	0,547
		50,0	3,90	0,545
		58,0	4,25	0,560
Dimethyl terephthalate*	$2\cdot10^{-3}$	34,5	14,6	2,50
		42,0	16,4	2,56
		50,0	18,0	2,52
		58,0	20,0	2,62
Nitrodimethyl terephthalate*	$1\cdot10^{-3}$	34,5	6,40	1,10
		42,0	6,80	1,05
		50,0	7,20	1,01
		58,0	7,80	1,03

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*First wave.

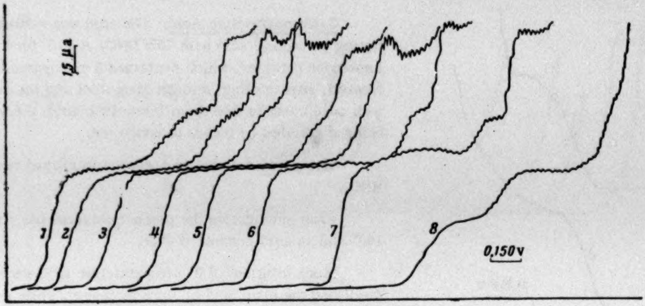

Fig. 6. Polarograms of dimethyl nitroterephthalate at a concentration of 1×10^{-3}M at various pH values of the supporting electrolyte. 1) pH 2.6; 2) pH 3.6; 3) pH 4.7; 4) pH 5.9; 5) pH 6.4; 6) pH 7.8; 7) pH 11.7.

We found that the wave of the ester is not clearly defined enough in acid buffer solutions.

It has been pointed out earlier [2] that the wave height in a supporting electrolyte of $(CH_3)_4NBr$ in 20% dioxane is higher than in a buffer solution. This led us to carry out a detailed investigation of the polarographic behavior of dimethyl terephthalate in methanolic solution in a supporting electrolyte of $(CH_3)_4NI$.

The characteristics of the polarogram of the ester are shown in Fig. 5.

The first wave with $E_{1/2} = 1.58$ v is of analytical interest. The height of this wave is proportional to the concentration over a very wide range (0.03-6.0 mM/liter). The diffusion current constant $I_D = 8.2 \pm 0.1$ μa/mM/liter (Capillary I).

Methyl Paratoluate. The methyl paratoluate used had a m.p. of 32-33°, and an ester number of 66.0.

Stock solutions were prepared in 100% CH_3OH, while polarograms were taken in 50% CH_3OH; 0.01 N $(C_2H_5)_4NOH$ served as the supporting electrolyte.

The characteristic shape of the polarogram is shown in Fig. 5. The wave obtained has $E_{1/2} = 2.12$ v. The relation between the diffusion current and concentration is linear.

The diffusion current constant $I_D = 2.9 \pm 0.1$ μa/mM/liter over the concentration range 0.1-8.0 mM/liter (Capillary I).

Dimethyl Nitroterephthalate. The ester used had a m.p. 75-76° and an ester number of 83.4.

Stock solutions of dimethyl nitroterephthalate were prepared by dissolving the nitro ester in 100% CH_3OH, while polarograms were taken in 40% CH_3OH.

Characteristic polarograms obtained at various pH values are shown in Fig. 6.

The one of greatest analytical interest is the first wave obtained at pH 3-7; this wave has a diffusion current constant which is independent of pH and has a half-wave potential $E_{1/2} = 0.20-0.45$ v.

There is a linear relation between concentration and diffusion current at pH 5.8 (Fig. 7) over the whole concentration range examined 0.02-8.0 mM/liter; the diffusion current constant $I_D = 6.1 \pm 0.1$ μa/mM/liter (Capillary I).

In conclusion we should like to point out that the linear relationship between the limiting current and the square root of the height of the mercury reservoir observed for all the compounds tested (Table 1), indicates that the limiting current has a diffusion character.

SUMMARY

A polarographic study has been made of terephthalic and paratoluic acids, nitroterephthalic and 2-nitroparatoluic

acids, dimethyl terephthalate, dimethyl nitroterephthalate, and methyl paratoluate. With the exception of dimethyl terephthalate this is the first time that these compounds have been studied polarographically.

All the test compounds, with the exception of paratoluic acid, are electrolytically reduced under certain conditions on a dropping mercury electrode to give clearly defined polarographic waves. Paratoluic acid can be rapidly and quantitatively nitrated to give polarographically active 3-nitroparatoluic acid.

The polarographic characteristics of the compounds mentioned above have been examined in aqueous solutions, and, in some case, in water-methanol solutions; it has been established that the limiting current has a diffusion character.

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A RAPID MERCURIMETRIC METHOD FOR THE DETERMINATION OF ISOBUTYLENE IN CRACKING FRACTIONS

S.M. Markevich, N.G. Polyanskii, M.M. Buzlanova, and E.D. Safronenko

Scientific-Research Institute of Synthetic Alcohols and Organic Products,
Novokuibyshevsk Branch

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Dobryanskii's sulfuric acid method [1] and modifications of this method [2] can be used for the determination of large amounts of isobutylene. Small amounts of isobutylene are determined by Denige's method [3-5], which is based on the formation of insoluble complexes of tertiary olefines with mercuric sulfate or nitrate. The precipitate which separates out is filtered off, carefully washed until the washings give a negative reaction for Hg^{2+} ions and then dried and weighed or dissolved in concentrated HNO_3 for subsequent thiocyanate titration [6-9]. We shall call the method involving dissolution and thiocyanate titration of the mercury sulfate complex of isobutylene [8] Method A for short, and that involving the mercury nitrate complex [7] Method B. Though these methods are accurate enough they are time-consuming.

The authors of the present article have developed rapid methods (C and D) based on precipitation of isobutylene with a known excess of standard solutions of $HgSO_4$ or $Hg(NO_3)_2$ respectively, dilution of the mixture obtained to a known volume with water or 0.25 N HNO_3, and a thiocyanate titration of aliquots of the supernatant solution. A solution of 33 g $HgSO_4$ in 20% H_2SO_4 [8] is used as the reagent in method C. An aqueous solution of $Hg(NO_3)_2$ with a concentration of 77 g/liter [7] is used as the reagent in Method D.

EXPERIMENTAL

The isobutylene used for preparing synthetic mixtures was obtained by dehydrating trimethylcarbinol in the presence of the sulfopolystyrene cation exchange resin KU-2 in the hydrogen form; β-butylene was prepared by dehydration of secondary butanol with sulfuric acid [9] and was freed from isobutylene which might be present as an impurity with 64% sulfuric acid. On the assumption that the α- and β-isomers behave identically in the test reactions, we shall refer to them in future as n-butylene.

A sample of C_4 hydrocarbon fraction was obtained from the absorption gas fractionation plant of the Novokuibyshevsk Oil Refinery and contained about 12% iso-C_4H_8; 29.8% n-C_4H_8 (total α- and β-butylenes); 13.0% of iso-C_4H_{10}; 39.3% n-C_4H_{10} and small amounts of C_3 and C_5 hydrocarbons present as impurities. The figures quoted were obtained by Dobryanskii's method [1] after low temperature fractionation.

Preliminary experiments, which had as their aim the establishment of the optimum conditions for the formation of precipitates of the complexes of iso-C_4H_8 with mercury salts, were carried out on mixtures of pure isobutylene and air. As a result of these experiments we abandoned the technique recommended in an earlier paper [8] of prolonged formation of the isobutylene complex with mercuric sulfate in the cold, and established that formation of a precipitate is complete in 10 min at 50°.

The isobutylene complex with $Hg(NO_3)_2$ is best formed on heating the test samples with the reagent on a boiling water bath for 15 min. When the isobutylene concentration of test mixtures is not too low, the precipitate with a stoichimetric composition which is formed with the $Hg(NO_3)_2$ solution is not corrected by addition of HNO_3 and NaOH [6]; the pH of such a reagent is 1.55 according to potentiometric titrations.

For the analysis of gas mixtures containing 2-20% isobutylene, 5-50 ml of reagent per 80 ml of test gas is used in method D, while 15 ml of reagent per 20-200 ml of gas is used in method C.

TABLE 1. Determination of Isobutylene by Methods A and C

Mixture No.	No. of determinations	Composition of the mixtures			Iso-C_4H_8 found, vol %		Experimental error (relative), %		Mean deviation of a single determination, %	
		Iso-C_4H_8	n-C_4H_8	Air	Method C	Method A	Method C	Method A	Method C	Method A
1	7	2,00	20,0	78,0	2,15	1,96	+7,5	−2,0	0,08	0,09
2	4	4,00	10,0	86,0	4,15	3,99	+3,8	0,0	0,08	0,12
3	7	9,80	27,5	62,7	10,2	10,0	+4,1	+2,0	0,12	0,13
4	4	12,50	12,5	75,0	12,3	12,3	−1,6	−1,6	0,12	0,16
5	4	19,20	9,6	71,2	19,7	19,6	+2,6	+2,5	0,27	0,27

TABLE 2. Determination of Isobutylene in Synthetic Mixtures by Methods B and D

Mixture No.	No. of analyses	Composition of the mixtures, vol %			Iso-C_4H_8 found, vol %		Experimental error (relative), %		Mean deviation of the measurements, %	
		Iso-C_4H_8	n-C_4H_8	Air	Method D	Method B	Method D	Method B	Method D	Method B
1	11	2,00	20,0	78,0	1,65	1,56	−17,5	−22,0	0,15	0,18
2	6	4,00	10,0	86,0	4,33	4,35	+ 8,3	+ 8,7	0,12	0,17
3	4	9,80	27,5	62,7	10,5	10,3	+ 7,2	+ 5,1	0,29	0,34
4	8	12,50	12,5	75,0	13,2	12,8	+ 5,6	+ 2,4	0.13	0,11
5	5	19,20	9.6	71,2	20,4	20,6	+ 6,2	+ 7,3	0,30	0,21

Determination of isobutylene by means of the mercuric salts reduces to the following operations.

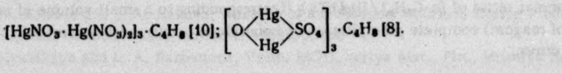
a) Determination of Isobutylene by Method C. A known volume of test gas supplied from a gas buret is passed for 15-20 min through a capillary into a test tube 20 cm long and 10 mm in diameter filled with a known volume of reagent. The test tube is then placed for 10 min in a water bath at a temperature of 50°. After the time indicated above has elapsed, liquid plus precipitate are quantitatively transferred to a 100 ml standard flask; water is used for washing the capillary and test tube. The contents of the standard flask are made up to the mark with water, and after the flask has been allowed to stand for one hour, a 20-25 ml aliquot is taken and treated with a saturated solution of $KMnO_4$ until a permanent rose color is obtained. Excess oxidizing agent is reduced with 2% H_2O_2, after which the solution is titrated with 0.1 N NH_4SCN.

b) Determination of Isobutylene by Method D. A known volume of mercuric nitrate is introduced into a 250 ml round-bottom flask. The flask is stoppered with a cork fitted with a three-way tap and is evacuated for 2-3 min using a prevacuum pump.

A known volume of gas is introduced from a gas buret into the evacuated flask, the flask is vigorously shaken for 5 min, it is then opened to the atmosphere and shaken again for a further 2 min; it is finally placed on a boiling water bath for 15 min. The mixture obtained is cooled, quantitatively transferred to a 250 ml standard flask, and its volume made up to the mark with 0.25 N nitric acid.

Twenty five ml of the supernatant liquid is taken, 1 ml of concentrated sulfuric acid, and 0.5 ml of a saturated solution of ferric ammonium alum are added, followed by a saturated $KMnO_4$ solution, until a bright-rose color is obtained. Excess permanganate is destroyed by addition of 2% hydrogen peroxide and the solution titrated with 0.1 N NH_4SCN.

Calculations of the isobutylene content of the gas mixtures were made on the assumption that one millimole of olefine in the complex with $Hg(NO_3)_2$ and $HgSO_4$ is equivalent to 6 mg-ion of Hg^{2+}. These relationships correspond to the following probable formulas of the precipitates:



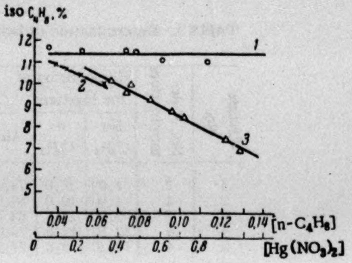
$$[HgNO_3 \cdot Hg(NO_3)_2]_3 \cdot C_4H_8\ [10];\ \left[O\genfrac{}{}{0pt}{}{\diagup Hg \diagdown}{\diagdown Hg \diagup}SO_4\right]_3 \cdot C_4H_8\ [8].$$

TABLE 3. Determination of Isobutylene in Production Fractions

Isobutylene content in the test sample, %	Isobutylene found (in %) by method:			
	C	D	B	A
12.1	11.8	11.6	11.3	10.4
6.0	5.9	5.6	5.6	5.4
1.2	0.96	0.96	0.96	0.93

A comparative evaluation of methods A, B, C, and D can be made on the basis of the results of the determination of isobutylene in synthetic mixtures containing air and n-butylene (Tables 1 and 2). Each result is the arithmetic mean of 4-11 determinations.

The results given in Table 1 illustrate that satisfactory agreement is obtained between the results for determination of isobutylene by means of methods A and C. The experimental error of method C increases with increasing relative content of n-butylene, which (though slowly) is also capable of reacting with $HgSO_4$ to form a sparingly soluble complex [8].



The effect of the value of the molar ratio $n\text{-}C_4H_8 : Hg(NO_3)_2$ on the results of determining isobutylene in synthetic gas mixtures. 1) Mixture of 11.3% iso-C_4H_8, 10% n-C_4H_8, and 78.7% air (upper scale); 2) mixture of 10.5% iso-C_4H_8, 27.5% n-C_4H_8, and 62.0% air (lower scale); 3) mixture of 10% iso-C_4H_8 and 90% n-C_4H_8 (lower scale).

It can be assumed that small amounts of this complex are coprecipitated with the corresponding derivatives of isobutylene, thereby increasing the amount of reagent used up in the reaction. Subsequent washing of the precipitate, presumably leads to partial dissolution of the complex of n-butylene with $HgSO_4$, and to a slight increase in the accuracy of the determination of isobutylene.

The reproducibility of the experimental results, which is characterized by the value of the mean deviation of one measurement, is almost the same in both methods.

The results given in Table 2 lead one to doubt Isakova and Rakhmanina's opinion [7] that mercuric nitrate is preferable to mercuric sulfate. Actually, on using a solution of $Hg(NO_3)_2$ as reagent, methods B and D give results which are less accurate and have a poorer reproducibility than methods A and C.

If it is assumed that buylenes with normal structure do not react with $Hg(NO_3)_2$ [6, 7], then the positive experimental errors can be related to occlusion of some of the reagent by the precipitate formed.

This treatment cannot, however, be extended to cover the analysis of mixture No. 1 with a low isobutylene content (2.00%) and a large excess of n-butylene, for which considerable negative errors are obtained.

The important question therefore arises: is it not possible to assume simultaneous formation of a soluble mercuric complex with n-butylene which complexes Hg^{2+} ions and displaces the equilibrium of the precipitation reaction $[HgNO_3 \cdot Hg(NO_3)_2]_3 \cdot iso\text{-}C_4H_8$ so that the precipitate dissolves? Such an assumption is confirmed by the results of a study of the relationship between the isobutylene content of different gas mixtures based on analytical results and the number of millimoles of n-butylene which are equivalent to 1 millimole of unreacted $Hg(NO_3)_2$ (diagram).

Curve 1, constructed on the basis of the analysis of mixtures with an almost equal content of isobutylene and n-butylene, exhibits the usual statistical scatter of experimental points determined by the reproducibility of the experiments.

Curves 2 and 3 show a definite trend in the experimental points, which indicates an increase in negative experimental errors with increasing relative n-butylene content (from 10 to 90 vol. %) and with increases in the ratio of the number of millimoles of n-butylene in a test sample to the number of millimoles of $Hg(NO_3)_2$ which do not react with isobutylene.

At low molar ratios of $[n\text{-}C_4H_8] / [Hg(NO_3)_2$/(corresponding to a small volume of test mixture or to a considerable amount of reagent) complete precipitation of isobutylene occurs, with occlusion of reagent leading to positive experimental errors.

At high molar ratios of $[n\text{-}C_4H_8]/[Hg(NO_3)_2]$ formation of a soluble complex of n-butylene with $Hg(NO_3)_2$ with simultaneous dissolution of the precipitate $[Hg\ NO_3 \cdot Hg(NO_3)_2]_3 \cdot C_4H_8$ is probable. These phenomena lead to incomplete precipitation of isobutylene, and, consequently, to negative experimental errors.

In order to prove formation of soluble complexes, the partition coefficients of Hg^{2+} ions between KU-2 resin in the H-form and a $Hg(NO_3)_2$ solution in the presence and in the absence of n-butylene were determined. K_D values calculated on the basis of the analytical results of equilibrium solutions [11] as the ratio of the number of meq Hg^{2+} calculated on one g of resin, to the number of meq Hg^{2+} in 1 ml of solution, were 5.80 and 9.84 respectively.

The decrease in the value of K_D in the presence of n-butylene is a direct indication of the formation of soluble complexes with $Hg(NO_3)_2$.

Similar phenomena are also possible during the interaction of n-butylene with $HgSO_4$. In the case of the analysis of small volumes of mixtures of 10% isobutylene and 90% n-butylene, coprecipitation of an insoluble complex of iso-C_4H_8 with the insoluble complex of n-C_4H_8 occurs, which leads to a positive experimental error. When a large volume of this gas mixture is analyzed (the same amount of reagent being used), the n-butylene present in excess can complex the mercury ions to form a soluble complex (which is titrated by the ammonium thiocyanate), which leads to dissolution of part of the precipitated complex of isobutylene with $HgSO_4$ and is responsible for the negative experimental error.

In future it will be necessary to undertake a systematic study of the conditions leading to the formation of, and the composition of the complexes of iso- and n-butylene with mercury salts and to correct the conversion factors included in the latest monographs [9, 10].

Until such work is carried out the methods which we have suggested can be used for determining isobutylene in mixtures which do not contain too high a percentage of n-butylene.

In order to check on the applicability of methods C and D to the analysis of industrial hydrocarbon mixtures, the isobutylene content of fractions from the absorption gas fractionation unit of the Novokuibyshevsk Oil Refinery was determined. Results of the analyses of the original fractions and of the same fractions after being diluted with air, by means of methods A, B, C, and D are compared in Table 3.

As the results in Table 3 show, the methods compared give results which are in agreement with each other. The time taken to carry out methods C and D is about a third of that required for methods A and B.

SUMMARY

A new, rapid method is suggested for the determination of isobutylene in its mixtures with n-butylenes; it is based on precipitation of the hydrocarbon to be determined with a known excess of a standard mercuric sulfate of nitrate solution, dilution of the mixture obtained to a known volume with water or 0.25 N HNO_3, and titration of an aliquot of the supernatant liquid with standard NH_4SCN solution. Precipitation of the complex of isobutylene with mercuric sulfate gives more accurate and reproducible results than those obtained when mercuric nitrate is used as precipitant.

The analytical methods developed have been used for determining the isobutylene in C_4 hydrocarbon fractions from the gas fractionation unit of the Novokuibyshevsk Oil Refinery.

Some suggestions are advanced re complex formation between n-butylene and mercuric sulfate and nitrate.

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BRIEF COMMUNICATIONS

INCREASING THE SENSITIVITY OF DETERMINATION BY MEANS OF A DISCHARGE IN A HOLLOW CATHODE

Yu. I. Korovin

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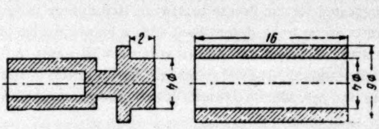
The sensitivity of the determination of many elements is very high when high temperature discharge conditions in a hollow cathode [1-3] are used as a light source. An attempt is made in this note to evaluate the limiting absolute sensitivity of the determination of various elements. The work was carried out on the setup described previously [1, 2]. The helium pressure in the discharge tube was 15 mm Hg, and the discharge current was 1100 ma. The design and dimensions of the graphite cathodes are shown in the diagram. A layter of polystyrene was deposited on the face of the capsule by evaporating a drop of a dichloroethane solution of polystyrene; a solution of the test element was then placed in the same position. After this solution had been evaporated, an outer cylinder was fitted onto the capsule and the cathode placed in the discharge tube. Requisite precautions for preventing accidental contamination were taken during all the operations. The results obtained, expressed in mμg (10^{-9}g), and also the corresponding results for the "copper spark" method and the fractional distillation method involving the use of a carrier [4] are given in the table. The analytical lines used are also included in the table. It should be borne in mind that the results relating to the last two methods were obtained by means of a Baird diffraction spectrograph, which has a considerably higher dispersion than the ISP-22 and ISP-51 spectrographs fitted with a UF-84 camera (the latter for determing sodium, lithium, and potassium) which we used. It can be assumed that the sensitivity with which lithium and elements whose analytical lines are located in the 2800-5000 A region can be increased (to differing extents for different elements) by using apparatus with a higher dispersion, and correspondingly more sensitive photographic materials.



The results given for a hollow cathode correspond to an increase of the blackening of the analytical line over the background of 0.05-0.10. Thus the sensitivity criterion for all the results included in the table is approximately the same. As these results show, the sensitivity of a determination by means of a discharge in a hollow cathode is in many cases considerably higher than in the most sensitive of the direct methods of spectrographic analysis. This fact can be used for increasing the sensitivity of analyzing pure solutions. The use of a discharge tube with a hollow cathode during the analysis of concentrates of impurities in chemicospectographic methods of analysis permits the sensitivity to be increased essentially in these cases also. The list of elements which can be determined in this way can be considerably extended.

In principle, the technique described should permit determination of all elements whose volatility (more accurately, the volatility of their appropriate compounds) under the specific conditions of a high temperature discharge in a hollow graphite cathode is close to the volatility of the elements included in the table. On the basis of the results obtained here one should be able to get an approximate idea of the sensitivity of determination which is attainable in these cases. The method suggested is, however, not suitable for the determination of many elements which form stable compounds with low volatility under the conditions described. In particular, the sensitivity of the determination of thorium, uranium, tantalum, niobium, tungsten, zirconium, and molybdenum proved to be very low. Photographs of the spectra of spark discharges using capsules as electrodes, showed that on treating the capsules in a discharge in a hollow cathode, the elements indicated remain almost completely on the surface of the capsules.

Element	Analytical line (A)	Sensitivity, mμg (10^{-9}g)		
		Hollow cathode*	"Copper spark"**	Fractional distillation with a carrier **
Al	1 3092,7	10^+	10	500
Ag	1 3280,7	0,03	—	5
B	1 2497,7	1	10	1
Be	11 3130.4	0.03	0,2	10
Cd	1 2288,0	30	200	7
Co	1 3453,5	0,3	50	100
Cr	11 2835,6	1	5	300
Cu	1 3247,5	0,03	—	30
Fe	11 2599,4	3	50	100
Ga	1 2943 6	0,03	100	—
K	1 7664,9	10	10	200
Li	1 6707,8	0,1	0,2	10
Mg	1 2852,1	$0,03^+$(~0,0001)	1^+(0,1)	50
Mn	1 2794,8	0,03	2	100
Na	1 5889,9	0,03	10^+	50
Ni	1 3050,8	1	10	200
P	1 2535,6	30	2000	5000
Pb	1 2833,1	10	5	100
Sb	1 2528,5	100	500	1000
Si	1 2881,6	1	10	300
Sn	1 2840,0	10	—	100
Zn	1 3345,0	3	200	2000

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* Absolute sensitivity when pure solutions were used.

* * Absolute sensitivity obtained by conversion from the concentration sensitivity for the main elements having a complex spectrum (100 mg U_3O_8· + Limit determined by impurities. The figures in brackets are limits which can be attained in the absence of impurites.

An interesting feature is that the sensitivity with which some elements (beryllium, silver, copper, manganese, gallium, sodium, and particularly magnesium) can be determined is fairly close to the theoretical limiting sensitivity for a discharge in a hollow cathode (10^{-13}g), calculated very roughly by Mandel'shtam and Nedler [5].

SUMMARY

The absolute values of the sensitivity of the determination of a number of elements using high temperature discharge conditions in a hollow graphite cathode have been established. The sensitivity with which most elements can be determined, with the exception of the least volatile ones, is considerably higher than the sensitivity which is possible when the same elements are determined by fractional distillation in a dc arc using a carrier, and by the "copper spark" method.

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NORMAL AND LOGNORMAL DISTRIBUTION OF RANDOM ERRORS IN QUANTITATIVE SPECTROGRAPHIC ANALYSIS

V.S. Urusov

Geochemical Institute of the Siberian Branch of the Academy of Sciences,
USSR, Irkutsk

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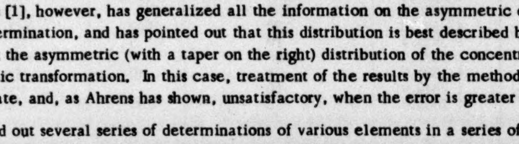
It is pointed out in textbooks on spectrographic methods of analysis that the distribution of random errors during the determination of the content of an element conforms to Gauss' normal law. This is in accordance with the well-known rule that the direct results of a physical experiment or measurement are subjected to the normally distributed random error. Ahrens [1], however, has generalized all the information on the asymmetric distribution of the errors in spectrographic determination, and has pointed out that this distribution is best described by the so-called lognormal law. This means that the asymmetric (with a taper on the right) distribution of the concentrations found becomes normal after a logarithmic transformation. In this case, treatment of the results by the methods of ordinary mathematical statistics is approximate, and, as Ahrens has shown, unsatisfactory, when the error is greater than ± 15%.

We have carried out several series of determinations of various elements in a series of samples – about 60 parallel determinations in each series. Curves constructed on the basis of the results of one series are shown in the diagram. The results of the other series are similar. In all cases the distribution of the concentrations measured (i.e. the distribution of the experimental error) approximates to a lognormal distribution (fig. c).



Distribution curves of the results of a spectrographic analysis. a) Antilognormal distribution of the blackening S; b) normal distribution of ΔS and log C; c) lognormal distribution of the concentration C.

The contradiction which arises can be eliminated, in our opinion, as follows.

As is known, the value of the concentration is found by means of the following formula:

$$\frac{S_1 - S_2}{\gamma b} = \lg C_1 - \lg C_2.$$

Here S_1 is the blackening of the analytical line, S_2 is the blackening of the line of the internal standard or background, γ is the contrast factor of the photographic plate (approximately 1), b is the selfabsorption coefficient of the line which is usually equal to one in the working region, C_1 is the concentration being determined, and C_2 is the concentration of the internal standard.

The blackening values S_1 and S_2 are measured directly and $\Delta S = S_1 - S_2$ is calculated. It is assumed that $\log C_2 = \text{const.}$ and a linear relationship is established between ΔS and $\log C_1$ (with a slope of γb).

In our experiments we studied the types of distribution curves for all the factors which enter into the formula indicated. We established that the distribution of S_1 and S_2 is antilognormal* (Fig. a), i.e., it is asymmetric, tapering to the left.

The distribution of S_1 and S_2 should correspond to the distribution of log C_1 and log C_2 (the correspondence being better the nearer γb is to 1). The distribution of the logarithms of the concentrations of the test element and the internal standard should also be antilognormal, and, consequently, the distribution of the concentration (i.e., the experimental error) should be normal, in complete accord with the assumptions of most spectroscopists.

Thus the distribution of log C_1 corresponds to the distribution of S_1, but not ΔS. ΔS – the difference between the two asymmetric distributions S_1 and S_2 – is an almost normal distribution** (Fig. b). It follows from this that when, using a linear curve (working), values of log C_1 are sought, which correspond, according to the basic formula, to ΔS values, one will inevitably obtain for log C_1 a distribution approximating to a normal rather than an antilognormal distribution for C_1 (since the logarithms of the concentration are distributed normally, Fib. b).

During treatment of several parallel results for one sample, one usually calculates the mean arithmetic value and the mean arithmetic or mean square error.

Nevertheless, a mathematical study of a lognormal distribution [2] shows that it is characterized by three different values – the mean arithmetic am, the mean geometric gm, and the most probable value y_{max}, between which the following relationships hold:

$$\lg am = \lg y_{\max} + 3{,}4539\lambda^2,$$
$$\lg am = \lg gm + 1{,}1513\lambda^2,$$

where λ is the mean square deviation of the logarithms of the values (distributed normally) from their mean arithmetic value. The latter corresponds to the mean geometric value of the lognormal distribution considered, not to its mean arithmetic value.

This means that the mean arithmetic value of ΔS corresponds not to the mean arithmetic value of C, but to their geometric value.

It can be shown that for an experimental error of, e.g., ± 5%, the mean arithmetic value will only exceed the mean geometrical value by about 0.1%, for an error of ±10% by about 0.5%, for an error of ±20% by 2%, and for an error of ±25% by 3%.

Thus the statistical error in the treatment of results has an essential effect only at high reproducibility errors (>10-15%).

A simple method can be suggested, however, whereby the error arising during calculation can be completely eliminated.

It must be borne in mind that as a result of the linear relation between ΔS and log C, the value of ΔS_{mean} corresponds accurately to log C_{mean}. This means that the correct value of C_{mean} corresponds to the antilogarithm of log C_{mean} and is the mean geometrical value for the lognormal distribution of C. This correct value of C is found more simply by calculating ΔS_{mean} and log C_{mean}. The experimental error can also be accurately calculated by means of the normally distributed values of ΔS or log C***.

For conversion from errors in the values of ΔS_{mean} or log C_{mean} to errors in the value of C_{mean} the following formula [3] can be used:

$$\varepsilon/C\% = 2{,}3\,\lambda \cdot 100,$$

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*The distribution of S is called antilognormal because the values of S from the formula $S = -\log a + 3 = \log {}^1/a + 3$ correspond to the antilogarithm of the values of I/a (a is the transmissivity), the distribution of which, as established in the same experiments, is normal.

**Under these conditions the distribution of ΔS will become closer to a normal distribution, the nearer is the distribution of S_2 to the distribution of S_1, i.e., the better the choice of internal standard or the better the continuous background "works" with the analytical line.

***The characteristics calculated for ΔS will be closer to the true value, the less the slope of the curve differs from 45° (i.e., γb from 1). Accordingly, it is more accurate to use the values of log C.

where ϵ /C% is the relative error for C_{mean}, and λ is the mean square error for ΔS_{mean} or log C_{mean}.

SUMMARY

The reason for the lognormal distribution of random errors during determination of the concentration of an element is discussed. It is shown that this phenomenon does not correspond to the physical nature of the spectrographic method, but is the result of the way in which spectrographic analysis data is treated. A method of eliminating the statistical error is suggested.

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DOUBLING OF THE MASS SPECTRUM OF CESIUM

M.P. Glazunov, V.A. Kiselev, and V.L. Litvakov

Institute of Physical Chemistry, Academy of Sciences, USSR, Moscow

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The technique most often used at present for obtaining ions during mass-spectrometric analysis of solids is ionization on an incandenscent surface. During the analysis of elements with low ionization potentials an ion source of this type is very efficient. The work was carried out with a ribbon type ion source which is part of the MS-4 mass-spectrometer. During the analysis of cesium isolated from the fission products of uranium 235, we observed doubling of the mass-spectrum of cesium; in addition to the main mass spectrum, a satellite spectrum (Fig. 1) appeared at a certain temperature of the ribbon source. This effect was observed when the temperature was increased considerably and when the ion source had been used for a long time with the test element. As the temperature increased the intensity of the peaks in the general mass-spectrum of cesium increased sharply (Fig. 2). The isotopic composition of cesium, calculated on the basis of the fundamental spectrum and on the basis of the satellite spectrum remained the same. We think that the mechanism of this phenomenon is as follows. The neutral cesium atoms evaporating from the ribbon when the source is operating condense on the colder parts of the source, including the edges of the lens slit standing close to the screen. During prolonged operation the edges of the slits of these lenses are strongly heated and when the temperature reaches about 500°, ionization of the cesium ions on this surface is possible. The ions formedwill have an energy differing from the energy of the ions formed on the ribbon itself by the value of the stretching voltage. They will be recorded as ions of lower mass. This explanation of the doubling effect can be confirmed by calculation.

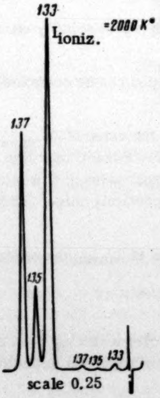

Fig. 1

The possibility of the appearance of additional peaks in the general mass spectrum, as the result of the formation of ions with a different energy, must be taken into account during the mass-spectrometric analysis of readily ionizable elements.

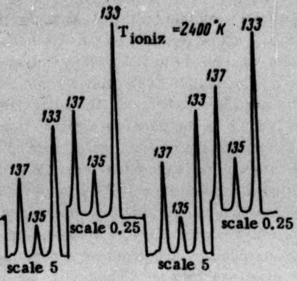

Fig. 2

SUMMARY

Doubling of the mass spectrum of cesium has been observed during the mass-spectrometric analysis of cesium isolated from the fission products of U 235.

It has been shown that this is the result of the ionization of cesium ions along the edges of the slit of the stretching lens.

DETERMINATION OF THE ISOTOPIC COMPOSITION OF OXYGEN IN SOLIDS

V.G. Finikov

Institute of Physical Chemisty, Academy of Sciences, USSR, Moscow

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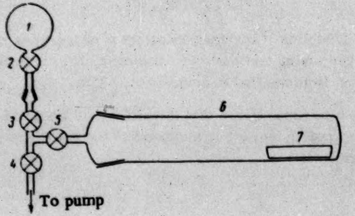
During studies of the isotopic exchange of oxygen in systems which include solids, the reaction kinetics in most cases are determined by the change in the isotopic compostion of the gas or liquid phase. Thermal or chemical decomposition methods, and also exchange with water are used for determining the isotopic compostion of solids. For mass-spectrometric measurements, the oxygen is usually converted into CO_2 (O_2 is used less frequently). In the case of thermostable materials or materials which exchange with difficulty however, these methods are not suitable. In addition, at low degrees of exchange, and when oxygen enriched to only a small extent with the heavy isotope is used, the error in determining the O^{18} content, as a result of dilution and side exchange reactions, is of the same order as the exchange effect it is desired to determine. When carbon is used as a reducing agent it must be borne in mind that at a reducing temperature in excess of 800° expensive apparatus is required, since in such cases quartz exchanges with CO_2 and O_2 at an appreciable rate.

Comparison of the Isotopic Composition of Oxygen in Some Solids as Determined by Gas Exchange and by their Reduction with $K_4[FE(CN)_6]$

Composition of the solid phase	Isotopic composition (in at. %) as determined by:	
	Gas exchange	Reduction of the solid phase
Al_2O_3	0,470	0,471
Li_2SO_4	0,328	0,332
$BaSO_4$	1,560	1,544
$Ba_3(PO_4)_2$	0,260	0,263
Na_2WO_4	0,250	0,254

Potassium ferrocyanide $K_4[Fe(CN)_6]\cdot 3H_2O$ has proved to be a very convenient reducing agent. By heating in a drying oven to 100° for a short time it is possible to prepare the very pure anhydrous salt, which, on heating above 400°, decomposes readily. The melt obtained, which contains finely divided carbon, is capable of reducing a wide variety of materials at a temperature of about 600°. The absence of oxygen in the reducing agent, and the low reducing temperature, eliminate the necessity of applying corrections to the directly measured isotopic composition of the oxygen in the CO_2 obtained. It is also possible to use quartz for making the requisite apparatus.

The apparatus used for preparing CO_2 samples during isotopic analysis of oxygen in solids of the oxide and salt type is shown in the diagram; it is simple to make and to operate. An aliquot of test salt or oxide (about 20 mg) is mixed with an equal volume of $K_4[Fe(CN)_6]$



Apparatus for preparing CO_2 samples during the isotopic analysis of oxygen in solids. 1) Receiver for CO_2 samples; 2-5) taps; 6) quartz test tube with a ground joint; 7) boat with aliquot of test material and $K_4[Fe(CN)_6]$.

and placed in a porcelain boat in a quartz test tube 6, whose volume should not be less than 30 ml. While the tube is heated with a gas burner to 150-200° the mixture is trained (aged) in a vacuum at 10^{-3}-10^{-4} mm Hg in order to remove traces of water and adsorbed air. The aging period is 10-30 min, and depends on the state of the preparation. Tap 5 is then switched over, the temperature is taken up to 600° and after 3-5 min with tap 4 closed the mixture of CO_2 and N_2 formed is transferred into receiver 1 provided with a standard ground joint which enables it to be connected to a mass-spectrometer. The accuracy with which the isotopic composition of oxygen can be determined depends on the quality of the mass-spectrometer. When solids are used in which the isotopic composition of the oxygen is not uniform with the depth of the crystals, the amount of $K_4[Fe(CN)_6]$ in the mixture must be increased, and complete reduction of the test material is achieved by increasing the heating time during decomposition.

The author has used this method for the analysis of the isotopic composition of oxygen in Al_2O_3, Na_2SO_4, $BaSO_4$, $Ba_3(PO_4)_2$, Na_2WO_4, Na_2MoO_4, and obtained very good results (see table).

SUMMARY

Most oxygen-containing solids can be reduced with $K_4[Fe(CN)_6]$ at temperatures below 600° in a simple quartz apparatus. The isotopic composition of CO_2 obtained agrees accurately with the isotopic composition of test materials obtained on complete reduction. The amount of test material required for analysis is 10-20 mg.

A RAPID METHOD FOR DETERMINING COPPER IN CADMIUM METAL AND CADMIUM SALTS BY MEANS OF POTASSIUM FERROCYANIDE

A.S. Kozlov

M.V. Lomonosov Moscow State University

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Methods used for the determination of copper in cadmium metal and cadmium salts include the dithizone extraction titration method [1], and photometric diethyldithiocarbamate method [2], and spectrographic methods [3]. Current standards, however, do not set a limit on the permissible amount of copper in many cadmium salts ($CdCl_2$, $Cd(NO_3)_2$, $Cd(CH_3COO)_2$ and $CdCO_3$) and only a qualitative test is given for copper, in which ammonia is used [4-7]. Since the methods mentioned above take a long time and cannot always be carried out in plant laboratories (e.g., the spectrographic method), while the ammonia method, in view of its low selectivity, should be replaced in the GOST methods by a better method, we thought that it would be expedient to describe in this communication a new, very simple, and rapid method for determining copper in cadmium and its salts.

The method is based on coprecipitation of traces of copper on cadmium ferrocyanide as collector [8], followed by a comparison of the intensity of the rose color of the precipitate with the colors of standard series of precipitates prepared under the same conditions, using the respective pure salts of cadmium to which copper has been added in the form of a standard solution.

Samples tested	Copper found, %	
	By the suggested method	By the dithizone method
Granulated cadmium metal ("analytical grade")	0.004	0.0045
Cadmium rods (K_DO grade)	0.003	0.0035
Cadmium metal (standard sample No. 177)	0.007	0.006
Cadmium chloride ("analytical grade")	0.0004	0.0005
Cadmium bromide ("analytical grade")	0.0004	0.0005
Cadmium iodide ("analytical grade")	0.0003	0.0004
Cadmium nitrate ("analytical grade")	0.0004	0.0003
Cadmium carbonate ("analytical grade")	0.0004	0.0004
Cadmium sulfate ("analytical grade")	0.0002	0.0003

On adding the first drops of $K_4[Fe(CN)_6]$ solution to a solution containing up to 100 mg Cd^{2+}, and up to 10 mg Cu^{2+}, up to 80% of the copper will be found in the $Cd_2Fe(CN)_6$ precipitate formed; as a result the precipitate is colored a weak rose-color (a precipitate of pure $Cd_2Fe(CN)_6$ is white in color). As the copper concentration in the original solution increases (when a constant amount of precipitant is used) the color intensity of the precipitate also increases. Coprecipitation of copper is greatest when the concentration of the cadmium salt is 1% and when a 0.5-1.0% $K_4Fe(CN)_6$ solution is used.

By varying the amount of solution and taking the minimum amount of precipitant, it is possible to determine down to 2×10^{-4}% copper; this means that it is possible to ensure control of the purest commercial cadmium salt available – chemically pure grade cadmium sulfate [2].

Analytical Procedure. 0.5 g of cadmium metal mark K_DO (or 0.25 g of mark K_D1 and K_D2) is dissolved on heating in a few ml of HNO_3 and the solution evaporated to dryness on a sand bath. The residue is transferred to a 100 ml standard flask and is made up to the mark with water. Twenty ml of the solution obtained is placed in a 25 ml cylindrical centrifuge tube with a spherical bottom and 0.5 ml of freshly prepared $K_4Fe(CN)_6$ solution added dropwise with continuous stirring. The liquid is allowed to stand for 10 min in order to allow the colloidal solution formed initially to coagulate, after which the precipitate is centrifuged for one minute at 1000 rpm. The solution is poured as completely free as possible from the precipitate, 2-3 drops of water are added and the precipitate stirred up until a homogeneous suspension is obtained. The precipitate is allowed to stand for 3-5 min, after which its color is compared with the colors of a standard series of precipitates prepared under the same conditions from samples of cadmium metal with a known copper content, or using reagent grade $Cd(NO_3)_2$ free from copper but to which known amounts of copper are added.

This method permits determination of down to 0.001% copper to cadmium metal. One determination takes 30 min.

If results are not required in the shortest possible time, the centrifuging stage can be omitted, and the precipitate simply allowed to settle. In such cases it is recommended that 60-110 ml tall cylindrical test tubes with spherical bottoms be used; 50-100 ml of solution containing 0.25-0.50 g of cadmium (mark K_DO or "analytical grade" material) is introduced into such test tubes, and from 0.5 to 2.0 ml of 0.5% $K_4Fe(CN)_6$ added. The test tube is stoppered with a cork, its contents carefully mixed and then allowed to stand for 3-4 hours. At the end of this period, without pouring off the solution above the precipitate, the test tube is rapidly rotated by hand, the tube being held in a vertical position and shaking avoided. During this operation the precipitate collects in the lower part of the test tube into a compact mass, and its color is compared in this form with the color of a standard series of precipitates prepared in a similar way. For convenience of observation it is recommended that a narrow movable mirror surface be fixed in the lower strip of a support. By lifting the test tube slightly and fixing the mirror at an angle to the observer, it is possible to examine the color of the precipitates easily.

Determination of down to 0.0002% copper in cadmium salts is carried out as follows.

One g of salt (weighed to an accuracy of 0.01 g) is dissolved in 100 ml of distilled water in a 150 ml beaker. From 5 to 10 drops (accurately) of 0.5% $K_4Fe(CN)_6$ is added with continuous stirring. The mixture is transferred as rapidly as possible into two 50 ml centrifuge tubes in which it is centrifuged for 5 min at 1500-2000 rpm. The solution is poured off almost completely from the precipitate, about 0.5-1.0 ml of centrifugate being left behind; the precipitate adhering to the bottom is stirred up to give a suspension in this volume. The suspension from both tubes is transferred into a 3-4 ml conical centrifuge tube and again centrifuged for one minute at 1000 rpm. The color of the precipitate, which has a volume of 20-30 mm^3, is compared with the color of a standard sample prepared at the same time as the test material and under the same conditions from the appropriate cadmium salt, containing a known amount (permitted by GOST specifications) of copper. For this purpose it is expedient to use a large diameter lens with a magnification of 2-3.

A determination takes 10-15 min.

A standard copper solution is prepared by dissolving electrolytic copper in HNO_3 (1:1); the solution is evaporated with H_2SO_4 to the appearance of white fumes, and the solution is finally transferred to a standard flask.

A stock solution of $K_4Fe(CN)_6$ is prepared by dissolving 50 g of its crystallohydrate in one liter of water. The solution will keep unchanged for several months in a dark vessel. 0.5% solution is prepared by appropriate dilution of the stock solution. The dilute solution will keep for 5-7 days.

The method developed for the determination of copper by means of $K_4Fe(CN)_6$ gives satisfactory results (see table) and can be recommended as a rapid method in technical analysis for controlling the production of cadmium metal and salts.

SUMMARY

A rapid method has been developed for the determination of copper in cadmium metal and cadmium salts. The method consists of the following: 0.5-1.0 ml of 0.5% $K_4Fe(CN)_6$ solution is added to a 1% solution of cadmium salt; the precipitate is centrifuged and the intensity of its rose color compared with the colors of a standard series of precipitates which are prepared under identical conditions.

The sensitivity of the method is for cadmium metal 0.001% of Cu and for cadmium salts 0.0002% of Cu.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

THE USE OF MAGNESIUM FERROCYANIDE FOR THE TITRIMETRIC DETERMINATION OF POTASSIUM IN PLANT MATERIALS

B.A. Gerasimov

Georgian Agricultural Institute, Tbilisi

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We recommend $Mg_2[Fe(CN)_6]$, which is superior to $Ca_2[Fe(CN)_6]$ used earlier [1], for the determination of potassium. SO_4^{2-} and small amounts of PO_4^{3-} ions do not interfere with determination of potassium by means of $Mg_2[Fe(CN)_6]$. It is prepared by adding an excess of an aqueous suspension of magnesium oxide to a washed precipitate of $H_4[Fe(CN)_6]$ obtained by adding concentrated HCl to a saturated solution of $K_4[Fe(CN)_6]$.

On adding ethanol to the aqueous solution containing potassium ions and excess magnesium ferrocyanide, the precipitate separates out rapidly and its composition corresponds accurately to the formula $K_2Mg[Fe(CN)_6]$.

Nevertheless, magnesium ions form precipitates of varying composition with potassium ferrocyanide under different precipitation conditions; thus when a solution of potassium ferrocyanide is added to an aqueous ethanol solution of a magnesium salt in the presence of excess potassium chloride, a precipitate of the composition $MgK_{10}[Fe(CN)_6]$ is formed [2].

The minimum ethanol concentration established empirically is 32% by volume. At higher ethanol concentrations, and when different precipitation conditions are used, the precipitate forms slowly [3]. At ethanol concentrations of about 50% the reagent itself starts to precipitate out, even in the absence of potassium ions; determinations are then impossible. It has been shown that potassium can be determined in the form of $5Cd_2[Fe(CN)_6] \cdot 4K_4[Fe(CN)_6]$ when pure salts are used [4, 5].

Potassium is determined as follows; a hydrochloric solution of the ash obtained from 3-10 g of organic material is prepared in the usual manner. The solution is transferred to a 25 ml standard flask and its volume made up to the mark.

Not more than 10-12 ml of solution containing 10-80 mg of potassium is taken for analysis; this amount is transferred to a test tube which has a mark at 15 ml, the solution is heated and neutral red added, MgO is then added in small amounts until the color of the solution changes from red to a weak yellow.

Calcium and magnesium phosphates are precipitated, as well as small amounts of Fe, Al, and Zn.

The solution is then allowed to become cold and its volume made up to 15 ml with water; it is filtered into a 15-20 ml measuring cylinder, 10-12 ml of this solution is poured into a test tube (fitted with a stopper) with a mark at 25 ml, and exactly 5 ml of 0.25 M $Mg_2[Fe(CN)_6]$ added (a more concentrated solution can be used, but in this case the volume of reagent added should be decreased accordingly).

After shaking, 8 ml of 96% ethanol is added, and, if necessary, water is added to bring the volume up to the 25 ml mark; the tube is shaken again and is then allowed to stand for 30 min for the precipitate to age. Four ml of water is added, or 3 ml if there is only a small amount of precipitate, the tube is shaken and the contents filtered through an

TABLE 1. Corrections to be Applied for the Precipitant Remaining in the Precipitate

Amount of potassium determined in the volume taken, mg	10	20	30	40	60	80
Amount of potassium that should be subtracted mg	1,4	1,70	1,60	1,50	1,30	1,00

Table 2

Taken	Potassium, mg				Taken	Potassium, mg			
	Found in the precipitates:					Found in the precipitates:			
	After washing		Without washing but after applying corrections			After washing		Without washing but after applying corrections	
15,0	14,7 14,9	14,8	15,7 15,9	15,8	50,0	50,1 50,3	50,2	49,0 50,8	49,9
25,0	25,0 24,4	24,7	25,5 25,7	25,6	75,0	75,1 75,3	75,2	77,1 76,2	76,6

ordinary filter paper 8 cm in diameter. The precipitate is quantitatively transferred onto the filter paper, using the filtrate itself, the filter plus precipitate are removed, placed on filter paper, and when the liquid has run off, they are pressed between sheets of filter paper until there is no observable trace of liquid on the paper; they are finally dried in a thermostat at 50-60° or in air until there is no odor of ethanol. The filter paper is opened out and immersed in a beaker containing 100 ml H_2O and 10 ml H_2SO_4 (1:3), the whole is then stirred with a glass rod until the precipitate dissolves; the solution is finally titrated with 0.05 N $KMnO_4$ until the color of the solution changes from yellow to brown; the color change at the end point is very sharp. One ml of 0.05 N $KMnO_4$ is equivalent to 3.91 mg potassium.

The precipitate obtained after squeezing out the liquid contains a small amount of precipitant which is titratable with $KMnO_4$, and accordingly the corrections given in Table 1 must be applied; it is also necessary to use filter papers of the same diameter (8 cm) made from ordinary filter paper.

The precipitate can be washed with a 10% solution of $MgCl_2$ in 32% ethanol; in this case there is no need to apply any corrections. This technique, however, leads to excessive use of alcohol, but the main disadvantage is that the time taken to carry out a determination is increased.

Table 2 contains results of the determination of potassium in synthetic mixtures of materials which occur in plant ash; the results were obtained on titrating washed and unwashed ferrocyanide precipitates with permanganate; in the latter case corrections were applied.

The experimental error does not exceed 6%. Ten potassium determinations can be carried out in 45 min.

SUMMARY

A simple method has been developed for the titrimetric determination of potassium in plant materials by means of magnesium ferrocyanide. The relative error for the determination of 10 to 80 mg of potassium does not exceed 6%.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

A TITRIMETRIC METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF VANADIUM

T.S. Zhigalkina and A.I. Cherkesov

Saratov Teaching Institute and the Astrakhan Technical Institute
of Fish Industry and Economy

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A large number of titrimetric methods are known for the determination of vanadium. One of the most widely used methods is titration of quinquevalent vanadium with Mohr's salt; vanadium is oxidized to the quinquevalent state by means of permanganate, excess of which is removed by boiling with concentrated HCl [1, 2], or with sodium nitrite [3, 4]; excess nitrite is complexed with urea. Oxalic acid is sometimes used for removing excess permanganate [5]. Diphenylamine and phenylanthranilic acid are the indicators most frequently used. Vanadium which has been reduced to the divalent state by means of cadmium amalgam can be titrated with dichromate [6] or trypan red [7]. In addition to direct titration, backtitration methods can also be used; vanadium is reduced with a known excess of Mohr's salt and the excess titrated with ceric sulfate in the presence of o-phenanthroline [4] or with dichromate in the presence of barium diphenylaminesulfonate [8].

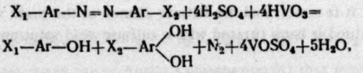
There is also a large number of potentiometric methods of determining vanadium [3, 5, 10-15]; the chemical processes underlying these methods are the same as those considered above. Nevertheless, none of the methods indicated above enable microgram amounts of vanadium to be titrated.

Tests which we have carried out showed that microgram amounts of vanadium can be titrated in an acid medium by means of azo dyes. A spectrophotometric variant for the determination of small amounts of vanadium by means of azo dyes has been described previously [9].

In acid media azo dyes form brightly colored addition products (halochromic compounds); the mechanism of this reaction reduces to an acid - base interaction of dye with acid; in this connection, azo dyes have found wide application as acid-base indicators (methyl orange, naphthyl red, methyl red, etc.). The azo group − N = N − is fairly active with respect to the action of reducing or oxidizing agents on it. In the first instance the reaction reduces to the formation of amino substituted azo- and diazocomponents:

$$\mathrm{Ar{-}N{=}N{-}Ar + 4H = Ar{-}NH_2 + H_2N{-}Ar}$$

In the second case oxidation − reduction splitting of the azo compound occurs with formation of hydroxy substituted azo- and diazo components and liberation of free nitrogen:



$$\mathrm{X_1{-}Ar{-}N{=}N{-}Ar{-}X_2 + 4H_2SO_4 + 4HVO_3 = X_1{-}Ar{-}OH + X_2{-}Ar{<}^{OH}_{OH} + N_2 + 4VOSO_4 + 5H_2O,}$$

where X_1 and X_2 are the substituting groups.

We should like to propose methyl orange (other azo dyes can be used also) as a titrant for the quantitative determination of microgram amounts of vanadium. The reaction between methyl orange and vanadate proceeds fairly quickly in a strongly acid medium (H_2SO_4 concentration equal to 60% by volume).

On titrating 10^{-6}M vanadate solutions with a methyl orange solution it was established that the stoichiometric coefficients are in the proportion of 4:1 (Table 1). When the reaction conditions are changed the ratio of the coefficients may be different (e.g.,6:1).

When chemically pure methyl orange and sulfuric acid are used the theoretical titer of methyl orange can be accepted; otherwise the methyl orange must be standardized against ammonium vanadate, or even better against vanadium

TABLE 1. Titration of HVO_3 with Methyl Orange (concentration of the solutions 10^{-4}M)

v_1, vanadate, ml	v_2, methyl orange, ml	v_1/v_2	v_1, vanadate, ml	v_2, methyl orange, ml	v_1/v_2
4,00	1,04	3,84	8,00	2,06	3.88
4,00	1,02	3,92	12,00	2,98	4,02
8,00	1,96	4,08	12,00	3,04	3,94

TABLE 2. Determination of Vanadium in Steel (Standard Sample No. 124, 0,240% V)

Vanadium found, %	Deviation, %	Vanadium found, %	Deviation, %
0,235	0,005	0,242	0,002
0,250	0,010	0,243	0,003
0,245	0,005	0,246	0,006
0,238	0,002	0,235	0,005

pentoxide. The methyl orange should be standardized with ammonium vanadate immediately after dissolving an aliquot of the dye in 60% sulfuric acid; this is necessary because in strongly acid media NH_4^+ ions are gradually oxidized by VO_3^- ions.

So that the ratio of the volumes of methyl orange and vanadate should be near to unity, 10^{-4}M solutions of methyl orange and approximately 4×10^{-4}M vanadate solutions should be prepared.

Titration is carried out with methyl orange supplied from a microburet (2-5 ml) until a stable weak rose color appears.

Forty micrograms of vanadium can be titrated with satisfactory accuracy without interference from the following ions (in μg): Co^{2+} –100, Ni_i^{2+} –400, Cu^{2+} –250, Cr^{III} –300, Al^{3+} –3000, Zn^{2+}–10,000, Mn^{2+} –2,000, Fe^{3+} –50 (in the presence of H_3PO_4–15,000) Ti^{IV} –50, MoO_4^{2-}, WO_4^{2-} –40. Fe^{2+}, Bi^{3-}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Br^-, NO_2^-, I^- and the oxidizing agents Cl_2, Br_2, $MnO_4^{\prime}$, $CrO_4^{\prime\prime}$ etc, interfere with titration.

The method suggested has been tried out on a standard sample of steel No. 124 (Table 2).

Determination of Vanadium in Steel. 0.1-0.5 g of steel is dissolved on gentle heating in a mixture of 20 ml dilute (1:3) sulfuric acid and 5 ml of dilute (1:1) nitric acid. The solution is evaporated until copious fumes of sulfuric acid are evolved; evaporation should not, however, be carried out until salts start to separate out. After cooling, the residue is diluted with 100 ml of water, 3-5 ml of phosphoric acid is added, and the vanadium is oxidized by dropwise addition of 2% potassium permanganate solution until a rose color which is stable for 1-2 min appears. After the vanadium has been oxidized, 1 ml of 4% manganese sulfate is added and the solution titrated with 0.1 N oxalic acid. The decolorized solution is filtered if it is turbid, and the filtrate diluted to the mark with water in a 200-250 ml standard flask. 2-3 ml of the solution obtained is back titrated with a sulfuric acid solution of methyl orange.

SUMMARY

A titrimetric method is suggested for the determination of microgram amounts of vanadium; it is based on the redox reaction of vanadium with methyl orange; the brightly colored sulfuric acid solution of methyl orange acts simultaneously as working solution and indicator. The concentration of the working solutions is of the order of 10^{-4}M.

The method has been checked on a standard sample of steel No. 124, and gave satisfactory results.

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DETERMINATION OF HEXAETHYL DILEAD IN TETRAETHYL LEAD

N. P. Lapisova and A. L. Gol'dshtein

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Even small amounts of hexaethyl dilead (HEL) present as an impurity in tetraethyl lead lead to instability of tetraethyl lead itself and of ethyl liquid prepared from it.

The following methods are known for the determination of HEL in tetraethyl lead.

1. Parallel use of the molybdate and iodometric methods with subsequent calculation of the amount of HEL [1]. This method is not suitable for technical control, since unsaturated organic products which can react with iodine may be present in technical tetraethyl lead.

2. Distillation of tetraethyl lead from its mixtures with HEL followed by determination of the latter on the basis of the specific gravity of the high boiling fraction remaining [2]. This method is complicated and involves numerous manipulations with such noxious materials as tetraethyl lead and HEL.

3. Determination of HEL in its mixtures with tetraethyl lead by spectrophotometric [3] and polarographic methods [4,5].

We have developed and checked on a method of determining HEL in tetraethyl lead which is based on the following reaction in acetone solution:

$$3Pb_2(C_2H_5)_6 + 2KMnO_4 \rightarrow 3Pb_2(C_2H_5)_6O + K_2O \cdot 2MnO_2$$

In developing this method we made use of Austin's observation [6] that tritolyl lead is oxidized by potassium permanganate with formation of the corresponding hydroxyl derivatives, and also of Bahr's observation [7] that triphenyl lead in the form of a suspension in acetone reacts quantitatively and instananeously with potassium permanganate, even at ordinary temperatures, to form the corresponding oxide. On the basis of this reaction Bahr suggested a method for the quantitative determination of triphenyl lead.

Experimental Part. HEL was prepared by Hein and Klein's method [8]. The HEL used was a transparent liquid with a lemon-yellow color and with a specific gravity of $d_{20}^{20} = 1.94\text{-}1.96$.

Tetraethyl lead was purified by two- and three-stream distillations of the technical product and had the following indices: specific gravity $d_{20}^{20} = 1.643\text{-}1.645$; $Pb(C_2H_5)_4$ content 99.0-99.8%.

Acetone conforming to GOST 2768-44 premier grade was used; it was freed from oxidizing impurities by boiling 600 ml of it with 20 g of potassium permanganate for 3 hr; it was finally distilled through a fractionating column.

Standardization of the Solution of $KMnO_4$ in Acetone. The most suitable solution proved to be a 0.05 N solution of $KMnO_4$ in acetone, i.e., 100 ml of solution contained 0.2634 g $KMnO_4$. The solution was standardized against oxalic acid in the presence of sulfuric acid. Nevertheless, in calculating the value of the normality under the titration conditions used in neutral and weakly alkaline media, the value of the normality obtained by the method given above was multiplied by 3/5.

HEL content of the tetraethyl lead, %	HEL taken, g	HEL found	
		g	% of that taken
26,57	0,2740	0,2733	99,7
2,93	0,1924	0,1957	101,7
0,0106	0,0018	0,0019	105,0

Study of the Interaction of Potassium Permanganate and HEL. A 0.08-0.2 g aliquot of HEL was placed in a 250 ml flask and 20 ml of purified acetone added; the HEL was then titrated with the acetone solution of permanganate with continuous stirring.

The reaction proceeds very rapidly – the permanganate color disappears immediately; the solution acquires a yellow color and becomes turbid. When titration nears completion, coarse, brown colored flocs which readily separate out are formed, and the solution becomes transparent. Titration can be considered complete when the liquid over the precipitate acquires a weak rose color on adding one drop of permanganate. On determining 0.1292 and 0.0944 g of HEL, values of 0.1320 and 0.0925 g were obtained.

HEL is therefore titrated completely; the deviation of the results obtained from the true value does not exceed 5%.

Behavior of Pure Tetraethyl Lead under the Condtions Used For Titrating with Permanganate. On adding the 0.05 N acetone solution of potassium permanganate to tetraethyl lead dropwise, the violet color disappears immediately, i.e. tetraethyl lead is oxidized. Nevertheless a different picture is observed when a dilute acetone solution of tetraethyl lead is used; the solution invariably acquires a rose color on addition of 1-2 drops of permanganate solution, this rose color being stable for 30 min and longer. This means that it is possible to determine HEL in tetraethyl lead by the method indicated.

Determination of HEL Present as an Impurity in Tetraethyl Lead. Solutions of HEL in tetraethyl lead were prepared for the work, the concentration of the former ranging from 0.01 to 26%. Five ml of solution (about 8.2 g) was taken for titration at concentrations up to 5%; smaller volumes of solution were taken at the higher concentrations. The sample was diluted with 20 ml of purified acetone and titrated with 0.05 N potassium permanganate with good stirring. The method permits determination of HEL with a relative error not exceeding 5% (see table).

A study was made of the effect of unsaturated organic compounds (which may be present in industrial tetraethyl lead) on the results of the determination of HEL in tetraethyl lead.

Olefines are oxidized by permanganate. On titrating a number of unsaturated compounds in acetone with permanganate, it was shown that oxidation is very slow. Since HEL, as noted already, is titrated immediately, then, as a number of tests showed, the presence of unsaturated organic compounds which react slowly with permanganate has almost no effect on the results of the determination of HEL.

Analytical Procedure: 5-10 ml of clear, sediment free technical tetraethyl lead is introduced into a flat-bottom flask; it is diluted with 20 ml of purified acetone, and is titrated with a 0.05 N solution of permanganate in acetone, the contents of the flask being mixed by a rotating movement. When the first 1-2 drops of $KMnO_4$ gives a rose color which does not disappear for 5-6 sec, it can be considered that there is no HEL in the tetraethyl lead. When the rose color disappears immediately, being immediately replaced by a yellow color, titration is continued until a rose color appears which is readily observable on a white background.

One ml of 1 N $KMnO_4$ is equivalent to 0.2944 g hexaethyl dilead.

SUMMARY

A method has been developed for the quantitative determination of hexaethyl dilead in tetraethyl lead in the presence of unsaturated hydrocarbons, the hexaethyl dilead being present as an impurity. The method consists in titrating an acetone solution of tetraethyl lead with a 0.05 N solution of potassium permanganate in acetone.

The experimental error of the method is 5-10% (relative). The method is sensitive down to 0.01%.

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REVIEWS AND BIBLIOGRAPHY

D. I. Ryabchikov and E. K. Gol'braikh, THE ANALYTICAL CHEMISTRY OF THORIUM

Moscow, Izd AN SSSR, 1960, 293 pp.

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pp 510-511, July - August, 1961

"The Analytical Chemistry of Thorium" by D. I. Ryabchikov and E. K. Gol'braikh, the book under review, is one of a series of monographs which the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR intends to publish under the general name "The Analytical Chemistry of the Elements." There is hardly any need to dwell on the very great necessity for and the very earliest publication of a series of monographs in which is brought together all the factual scientific-methodological material and the vast practical experience accumulated by many thousands of research and practical workers in the field of analytical chemistry both in the USSR and abroad. Such an analytical encyclopedia will favor the further development of this important branch of science, and its practical application to solving all the complex problems in the field of the analytical control of modern production.

The fact that the authors used 2142 literature sources published in the USSR and abroad during 1957-1958 testifies to the huge amount of work carried out by them in compiling this monograph.

The monograph comprises five chapters.

The first is devoted to information on the general and inorganic chemistry of thorium.

The second chapter is devoted to descriptions of the chemical and physicochemical methods of determining thorium, these being prefaced by qualitative reactions for the thorium ion.

A considerable amount of attention is given to the complexometric method, which can be regarded as a fundamental method. Questions relating to the theory of complexometric titration and the indicators used are considered here, and actual methods of determining thorium are described. Titrimetric, spectrophotometric, and volumetric high frequency methods of determining thorium by means of sodium ethylenediamine tetracetate are also described.

Consideration of photometric methods of determining thorium is preceded by an outline of some general theoretical premises relating to the development of colored reaction products formed during the interaction of thorium ions with organic and inorganic reagents.

It is pointed out that polarographic methods of determining thorium have not found practical application. An indirect amperometric method of determining thorium is described. Spectographic, x-ray spectographic and radiometric methods of determining thorium are briefly outlined.

Separation of thorium from accompanying elements forms the subject of the third chapter.

For separating thorium from the rare earths, use is made of methods based on differences in the chemical and physical properties of these elements (basicity, solubility of their respective compounds, their complex-forming capacity etc). Chromatographic, extraction and other separation methods are considered.

In addition, methods are described for separating thorium from scandium, titanium, zirconium, uranium, iron, aluminum, niobium, tantalum, silicon, and phosphorus and from lead and other metals of the hydrogen sulfide group.

The fourth chapter is devoted to methods of determining thorium in natural and industrial materials, including alloys. Regeneration of thorium from industrial wastes is also described.

Methods of determining impurities in technical and high purity thorium are considered in the fifth chapter. Methods of purifying thorium from uranium-233, protoactinum-233, and radioactive fission products are also described in this chapter.

Of considerable use are the literature references on the synthesis of the various reagents required for carrying out a particular method of analysis; this will help our analysts to make wider use of new analytical methods for determining thorium.

Though this review of the contents of the monograph is of necessity brief, it nevertheless gives a fair idea of the huge amount of material that it contains.

Bearing in mind the fact that many, if not most of the reagents, and the conditions under which they are used, turn up during consideration of the methods of determining thorium (Chapter II), during consideration of the methods of separating thorium from other components (Chapter III), and also during consideration of methods for determining thorium in natural and industrial materials (Chapter IV), it does strike one that it might be better to bring together all three applications of any reagent that turns up repeatedly in the general theoretical part of the monograph, with the aimof greater compactness and for making it easier for the reader to obtain the information he wants on any particular reagent he is interested in. There is the possibility, however, that should this be done, it might be difficult to achieve the requisite separation of the fundamental analytical methods, and to deal with them sufficiently fully.

Moreover, in order to avoid frequent repetition, resort should be made more often to reference to previous sections of the monograph in which any particular reagent or method has already been dealt with.

A large number of methods for determining thorium and the reagents used for this purpose, are described in the mongraph, and the sensitivity, accuracy, and effect of other elements are considered; methods of removing the latter are also included. Many of these methods are very similar to each other with respect to these analytical characteristics, i.e., sensitivity, etc. Accordingly, it is very difficult for the analyst who is making his first acquaintance with the analytical chemistry of thorium to assimilate, critically evaluate, and select the best method from the vast amount of material collected in the book under review, without having the general characteristics, and a comparison of the advantages and disadvantages of each method before him.

In order to get a more rapid idea of the advantages of some methods and the drawbacks of others, it would obviously be very useful to include tables at the end of each chapter (or in the appendix) containing the most important characteristics of the methods with respect to their fundamental indices.

Having completed an examination of this monograph, the reviewer must express the great satisfaction which he had derived in reading it. This monograph on thorium is a serious contribution to Russian literature on the analytical chemistry of the elements, it will be of great service to analytical chemists in scientific-research and industrial laboratories.

One must express the hope that the material in the reviewed monograph (just like that in the other monographs in this series of the "Analytical Chemistry of Elements") will be periodically supplemented by systematic critical reviews of the literature.

A. M. Dymov

G. Charlot, LES MÉTHODES DE LA CHIMIE ANALYTIQUE ANALYSE QUANTITATIVE MINÉRALE

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pp 511-512, July-August, 1961

G. Charlot's book consist of two parts.

The first part is devoted to the theoretical bases of analytical chemistry. The material is classified as follows: 1) chemical reactions in solution; 2) electrochemical reactions and voltametry; 3) measurement methods; 4) various methods and techniques.

The second part is devoted to selected methods of determining a large number of elements, methods which have not only been tried out in the author's laboratory, but also by the Commission on Analytical Methods of the Commissariat on Atomic Energy, by the French Standardization Association, by the analytical chemistry section of the French Chemical Society, and also by some industrial societies. Methods of determining all the elements with the exception of the inert gases and radioactive elements (apart from Tc, Th, and U) are considered in this part.

In Section I of the first part, the reactions of acids and bases, oxidizing agents and reducing agents, and precipitation reactions (including homogeneous precipitation) are considered in general terms; the concepts of extraction and its practical application, distillation, and coprecipitation are advanced; various types of chromatographic techniques and their practical application are considered. In addition, the dissociation constants of acids and bases, the apparent instability constants and the redox potentials are included.

Section II is devoted to a qualitative and quantitative interpretation of the results of electrochemical reactions and to the theory of electrolysis. The nature of the current - potential curves is discussed, as well as the effect on them of various factors in the course of chemical reactions when various electrodes are used; the techniques of the practical use of electrolysis and electrography and reduction by metals and amalgams are discussed.

The theoretical bases of various methods used in analytical chemistry are outlined in Section III, and these methods include spectrophotometric, luminescent, thermogravimetric, radiometric, etc. Various titrimetric methods are considered: potentiometric, amperometric, coulometric, photometric, radiometric, complexometric tensiometric, and many others. The material on polarography is presented in the chapter devoted to amperometry. Both widely used, as well as new reagents and indicators used for pH determination in redox reactions,etc are discussed. Finally the bases of emission spectrographic analysis and spectrophotometry are outlined.

Section IV is devoted to the properties of ionizing and non-ionizing solvents, and their practical use in neutralization, complex formation, and redox reactions.

Chapter V is devoted to the question of determining traces of elements, preparation of samples, dissolution of samples, and the destruction of organic materials by wet and dry methods. In addition, the sensitivity limits of the methods are given. In the sections devoted to the analysis of gases, and also to those on semimicro- and microdeterminations the author limits himself to published sources.

The characteristic way in which the material is outlined in this interesting book distinguishes it from other textbooks on analytical chemistry. It has been written very clearly, the newest scientific data being taken into account. Complexometry, titration in nonaqueous media, electrochemical reactions, various new titration techniques—thermochemical, polarometric, refractometric, cryometric, gasometric— electrochromatography, spectrophotometric titration, statistical treatment, microbiological analysis,etc are all well treated. Particular attention has been given to the quantitative determination of such elements as U, Th, Ti, Zr, Nb, Ta, B, Be, etc.

The textbook includes 392 diagrams, many of which are original and illustrate the theoretical material graphically. References to published original work and reviews are included in each chapter.

It would be correct to say however (incidentally,with G. Charlot's agreement) that the book is not perfect. Subjects of similar themes are separated in many instances. We think that questions relating to the theory of electrochemical reactions and voltametry should not be separated from amperometric, potentiometric, and similar analytical methods. Material on radiometric determination should be linked with the expostion of radiometric titration. Methods of separating and methods of determining the elements should be separated more clearly. One must regret that physical methods of analysis are hardly dealt with at all.

On the whole G. Charlot's book is, undoubtedly, of great interest not only for analytical specialists, but can also serve as a reference book and textbook for aspirants and students,and should be translated into Russian.

D. I. Kuznetzov

A NEW REAGENT FOR THE DETERMINATION OF CADMIUM - BROMBENZTHIAZO

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back cover, July-August, 1961

A new reagent for the colorimetric determination of cadmium ~brombenzthiazo~ has been synthesized at the All Union Scientific-Research Institute of Chemical Reagents and Special High Purity Chemicals (IREA).

The new reagent has approximately the same sensitivity and selectivity as dithizone, but has the advantage over the latter that it is simpler to use and is more stable.

Organizations and enterprises wishing to test the new reagent may obtain a free sample, and instruction for its use, by applying to the address: Moscow E-61, Bogorodskii Val, D. 1, IREA. It is requested that a report on the practical value of the new reagent be sent to IREA within a two month period after receiving the reagent.

The Institute will advise on all questions relating to the use of brombenzthiazo.

THE PART PLAYED BY ZIMMERMAN-REINHARDT MIXTURE IN THE PERMANGANOMETRIC DETERMINATION OF IRON

O. A. Songina and S. A. Khodasevich

Kazakh State University, Alma-Ata

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During titration of iron with permanganate in a hydrochloric acid medium, Zimmerman-Reinhardt solution (we shall henceforth refer to it as Z. R.) which contains manganese sulfate, sulfuric and phosphoric acids is used. Oxidation of chloride ions by permanganate interferes with titration of iron with permanganate in a hydrochloric acid medium when this mixture is not used. The theoretical basis of the action of Z. R. mixture is still the object of discussion. It has been assumed as a basis that oxidation of chloride ions by permanganate is induced by Fe^{2+} ions, while Zimmerman [1a] in 1882, and subsequently Mansho [1b, 2, 3] suggested formation of an intermediate compound of iron which possesses a higher oxidizing capacity than permanganate; this iron compound (assumed to be Fe_2O_5), on breaking down gives "active oxygen" which then reacts with the chloride ions; when Mn^{2+} ions are then introduced into the solution, the "active oxygen" reacts with them, and not with the chloride ions, to give manganese dioxide which behaves as an oxidizing agent with respect to Fe^{2+} ions. Shilov [3] has referred to Wagner's work [4] on the coupled oxidation of hydrochloric acid during the reaction between permanganate and divalent iron; Wagner assumed that oxidation of chloride ions is a side reaction following upon the formation of ferrohydrochloric acid. Shilov on the other hand is of the opinion that oxidation of chloride ions by permanganate in the presence of Fe^{2+} is a typical case of chemical induction, and that the question of whether this process is the main or side reaction depends on the ratio of the concentrations of the acceptor and inductor.

Having considered, and experimentally checked Mansho's hypothesis re the formation of a higher oxide of iron, Shilov arrived at the important conclusion that the active product may be formed not only from the inductor, but also from the actor, if the process does not go to completion i.e., to the most stable oxidation state, but stops at some compound "in an intermediate oxidation state," which on breaking down into compounds of higher and lower oxidation states, behaves as a stronger oxidizing agent than the original material.

This assumption of Shilov has been developed subsequently by many research workers. Thus Basset [3] is of the opinion that there is no need to refer to the formation of a hypothetical compound of iron in a higher valence state, when the whole process can be explained by stepwise reduction of permanganate by Fe^{2+} ions, leading to formation of Mn^{3+} which is also an oxidizing agent with respect to chloride ions; the addition of Mn^{2+} ions lowers the oxidation potential of Mn^{3+} to such an extent that oxidation of chloride ions does not occur. Schleicher in some interesting papers which appeared during 1955 and 1958 [5, 6] develops some ideas which coincide almost completely with N. A. Shilov's hypothesis (Schleicher does not, however, refer to Shilov's work). Schleicher's ideas are almost purely physical in character, and he compares the induction of a chemical reaction with the phenomena of selfinduction and induction which occur in the first order reactions. Schleicher emphasizes that, from a chemical point of view, the phenomenon of selfinduction is a disproportionating phenomenon, and that during redox reactions magnetic fields are formed whose intensity is determined by the number of electrons participating in the process; the existence of these fields and the increase in their intensity which occurs on introducing an additional noninhibited electron process determines the course of the whole redox process. In the given instance, the role of the additional agent is played, according to Schleicher, by the Mn^{3+} ion which is formed reversibly from Mn^{2+} ions and participates in the oxidation of the iron. Since each permanganate ion gives, in the final count, only one Mn^{2+} ion, then in order for the oxidation of iron to proceed sufficiently rapidly, a sufficient amount of Mn^{2+} ions must accumulate, or they must be added specially, this being the case when Z.R. mixture is added. Schleicher considers that the potential of the system Mn^{3+}/Mn^{2+} is less positive than the potential of the system MnO^-/Mn^{2+}, but close to it, accordingly oxidation of chloride ions does not occur, and oxidation of iron is not hindered.

Papers were published by Japanese workers in 1959 [7]. It is difficult to judge whether these authors were aware of N. A. Shilov's work but they advance ideas exactly similar to those of N. A. Shilov, i.e., formation of an active agent from the actor. The Japanese workers have introduced a new term "inductive actor" and are of the opinion that in the system $MnO_4^- - Fe - HCl$, these actors are ions of sexi- and quinquevalent manganese which oxidize the chloride ion to ClO^-; the Mn^{2+} ions introduced with the Z.R. mixture lead to rapid disappearance of these ions as a result of their reduction to Mn^{IV} and Mn^{III}.

In 1954 Schäefer published a paper [8] on experiments which he carried out to demonstrate the effect of Fe^{2+} and Mn^{2+} on oxidation of chloride ions by permanganate. His apparatus consisted of two flasks connected in series with each other; one of these flasks contained a solution of permanganate in hydrochloric acid, while the other contained a solution of potassium iodide and starch. When a stream of nitrogen was passed through the first flask, the solution in the second flask remained colorless; accordingly, the permanganate did not oxidize chloride ions. When a small amount of Fe^{2+} was added to the contents of the first flask, within 10 min, the solution in the second flask acquired a blue color. When, in addition to Fe^{2+}, Mn^{2+} was also added to the contents of the first flask, the solution in the second flask did not turn blue; this indicated that in the presence of Mn^{2+}, chloride ions are not oxidized by permanganate. Schafer makes the important point that when the hydrochloric acid concentration is greater than 0.5 N, direct reaction between permanganate and chloride ions proceeds even in the absence of Fe^{2+} ions.

In order to study the reaction between permanganate and iron we adopted an amperometric method,* using the usual setup with a rotating platinum electrode and a mercury-iodide reference electrode [9]; the potential values given below are referred to this reference electrode (the potential of the mercury–iodide electrode is +0.02 v).

First we "titrated" the supporting electrolytes with permanganate solution (0.05 N) at a potential of +0.7 v, which corresponds to the region for the diffusion current of the reduction of permanganate [9]. Such a technique makes it possible to assess whether any reaction occurs between permanganate and the solution to which it is added. The curves obtained are shown in Fig. 1: curve 1 shows that as the permanganate concentration increases in the supporting electrolyte of sulfuric acid, the current increases linearly (equation $i_d = KC$); this indicates that there is no chemical interaction between permanganate and the supporting electrolyte. Curve 2 (Fig. 1) was obtained for the same sulfuric acid supporting electrolyte, but with addition of hydrochloric acid. In this case the current increases somewhat more slowly and deviates from the straight line $i_d = KC$. This is explained by an interaction between permanganate and hydrochloric acid, which increases with increasing permanganate concentration. As pointed out above, Schäefer [8] has shown that direct (not induced) interaction of permanganate with hydrochloric acid is observed even in the absence of Fe^{2+} ions when the hydrochloric acid concentration exceeds 0.5 N (in our experiments the hydrochloric acid concentration was about 1.5 N, while the total acidity of the solution was about 5 N).

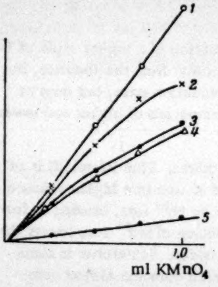

Fig. 1. Titration of supporting electrolytes with permanganate at 0.7 v. 1) Sulfuric acid; 2) sulfuric acid + hydrochloric acid; 3) sulfuric acid + + manganese sulfate; 4) sulfuric acid + hydrochloric acid + + manganese sulfate; 5) Z.R. mixture + hydrochloric acid.

We then titrated solutions of sulfuric acid and mixtures of sulfuric and hydrochloric acids to which were added a small amount of manganese sulfate (curves 3 and 4, Fig. 2). During these titrations, the current which increased immediately on adding each portion of permanganate, decreased with time, and reached a constant value after 30-60 sec (in order to avoid making the diagram too complicated, we have only given the stable current values). The comparatively slow rate at which the current is established indicates a slow reaction between permanganate and Mn^{2+} ions. Shilov has already remarked on this point [2]. The solution acquires a reddish tinge characteristic of Mn^{3+} ions. The fact that the current does not drop to zero but has a definite final value, indicates that the product of the reaction described is capable of being reduced on a platinum electrode at the potential of +0.7 v at which titration is carried out. Since both curves almost coincide (curves 3 and 4, Fig. 1), it is obvious that in both cases – with and without hydrochloric acid – the same process occurs, i.e., oxidation of Mn^{2+} ions by permanganate to Mn^{3+}.

We should like to point out that Selim and Lingane [10] have described a method for producing Mn^{3+} ions by direct titration of divalent manganese with permanganate in a sulfuric acid medium: $Mn^{VII} + 4Mn^{2+} \rightarrow 5\,Mn^{3+}$; formation of Mn^{3+} was established on the basis of a spectrophotometric study of the solutions.

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* M. R. Dausheva who carried out all the control tests on titration and polarographic determination helped us considerably in the experimental work.

Figure 1 also includes a titration curve of Z.R. mixture with permanganate (curve 5); in this case again the current is not established immediately; fairly stable values are obtained for the current after 20-30 sec, these values being strictly proportional to the amount of permanganate added. The solution acquires a cherry-red color.

Divalent iron (Mohr's salt) was then titrated with permanganate in the same supporting electrolytes. As Fig. 2 shows, titration in a sulfuric acid supporting electrolyte (curve 1) proceeds without any complications; after the end point, the solution has the rose-violet color characteristic of permanganate. When hydrochloric acid is present (curve 2) the titration curve is "saw-toothed" in shape—after addition of each portion of permanganate the current first increases and then rapidly drops, while the permanganate color disappears and a chlorine odor is observed. It is quite obvious that under such conditions visual determination of the end point is impossible. The interaction between permanganate and hydrochloric acid, as pointed out already, is observable even in the absence of iron; in the presence of the latter the reaction proceeds more intensely because of the Mn^{3+} ions formed from Mn^{2+} ions which appear in solution as a result of the oxidation of the first portions of Fe^{2+} by permanganate. The upper points on curve 2 (Fig. 2) are plotted approximately, since it was impossible to fix their positions accurately: the current drops very rapidly to reach a low constant value which increases slightly as titration proceeds. This current is determined by electrode reduction of the free chlorine which gradually accumulates in the solution.

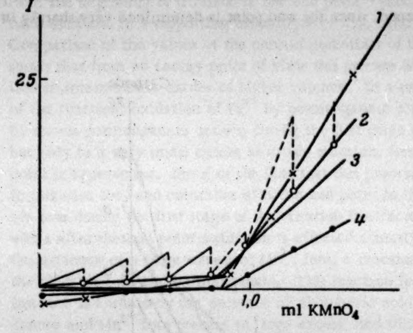

Fig. 2. Titration of divalent iron in different supporting electrolytes. 1) Sulfuric acid; 2) sulfuric acid + hydrochloric acid; 3) sulfuric acid + hydrochloric acid + manganese sulfate; 4) Z.R. mixture + hydrochloric acid.

When manganese sulfate (curve 3) or Z.R. mixture (curve 4) is added to the hydrochloric acid solution of Mohr's salt being titrated, titration proceeds completely normally. The only difference between the curves obtained in this case and when pure sulfuric acid is used as the supporting electrolyte is the lower value of the current after the end point — just as in the case of curve 5, Fig. 1. When only manganese sulfate is present, the solution acquires an orange-red shade, while in the presence of Z.R. mixture it is cherry-red in color. As long ago as 1905, Shilov pointed out that the first product from the reduction of permanganate is manganese oxide Mn_2O_3, which gives a very stable red colored solution with complexing agents. In our case, working with Z.R. mixture, phosphoric acid plays this part. The complex compounds of Mn^{3+} with phosphoric and pyrophosphoric acids have been described several times in the literature [3, 11, 12]. Formation of the phosphate complex of Mn^{3+} also explains the drop in the current which we observed after the end point (compared with the current in the absence of Z.R. mixture); this is obvious when a comparison is made of the polarograms of permanganate in a supporting electrolyte of sulfuric acid (curve 1, Fig. 3) and in a supporting electrolyte of Z.R. mixture (curve 2). According to Belcher and West's results [13] the potential of the pyrophosphate complex of Mn^{3+} (for equimolar ratios of Mn^{2+} and Mn^{3+}) is +1.22 v, consequently Mn^{3+} ions in the presence of phosphate cannot be an oxidizing agent for chloride ions.

Naturally, hydrochloric acid modifies the shape of the permanganate polarogram in the presence of Z.R. mixture, since the anodic current for the oxidation of chloride ions (curve 3, Fig. 3) appears, but even in this case oxidation of chloride ions by trivalent manganese is excluded: this is clear from a comparison of the potentials at which the curves intersect the abscissa in Fig. 3.

Earlier we were able to show that the reaction rate between permanganate and Fe^{2+} ions is greater than that between permanganate and Mn^{2+} ions [12]. Shilov and other workers [1b] have remarked on the relative slowness of this reaction in acid media. Since in our case the acidity of the solution was fairly high (about 5 N), it is only natural to postulate that oxidation of Fe^{2+} occurs first. But, even if it is assumed that the reaction $Mn^{VII} + 4Mn^{2+} \rightarrow 5Mn^{3+}$ proceeds simultaneously with oxidation of iron, it still does not alter the position and is not reflected in the titration results, since the Mn^{3+} formed is immediately reduced by Fe^{2+} ions, i.e., the process postulated by Schleicher occurs [5, 6].

It is usually accepted that the end point of titration of divalent iron by the Z.R. method coincides with the appearance of the red-violet color of permanganate. In actual fact it is the cherry-red color of the phosphate complex of Mn^{III} which serves as an indicator of the end point. This is a fact which can be readily established even by a visual comparison of the color obtained during such a titration, with the color of a permanganate solution of the same concentration. The high results which are obtained when the usual visual method is used, and which are referred to in textbooks on quantitative analysis [15], are explained, not by the fact that the "oxidation products (i.e., chlorine or hypochlorous acid) react incompletely with divalent iron" [14], but by the fact that the color of Mn^{3+} is considerably less intense than the color of permanganate, so that titration is carried on to a further stage than is necessary until the solution has a clearly defined color. The slow titration recommended in textbooks [15] finds an explanation in the slowness of the reaction between Mn^{2+} and permanganate mentioned above. Using an amperometric method, however, it is also possible to titrate iron in a hydrochloric acid medium with reasonable accuracy, not only in the presence of Z.R. mixture, but even in its absence, since the end point is determined very sharply in this case too.

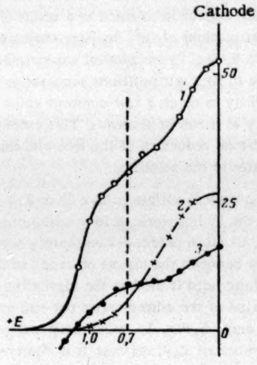

Fig. 3. Polarograms (on a platinum electrode). 1) Permanganate in a sulfuric acid supporting electrolyte; 2) permanganate in a supporting electrolyte of Z.R. mixture; 3) permanganate in a supporting electrolyte consisting of Z.R. mixture and hydrochloric acid. The permanganate content was the same in all cases — 0.6 ml of 0.05 N permanganate in 20 ml.

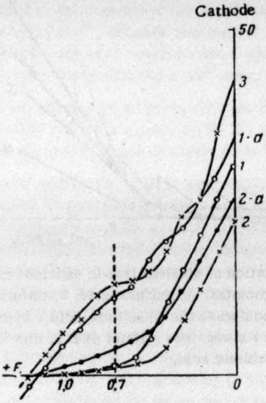

Fig. 4. Polarograms taken during titration of iron with permanganate. 1,2) Before the end point: 1) in a supporting electrolyte of sulfuric and hydrochloric acids; 2) in a supporting electrolyte of Z.R. mixture and hydrochloric acid; 1a and 2a) in the same solutions after the end point in the presence of excess permanganate (0.2 ml of 0.05 N permanganate); 3) chlorine water + Fe in a supporting electrolyte of sulfuric acid.

The amperometric method, in contrast to the usual method, allows one to follow the processes which occur in solution during titration, and which are reflected in the behavior of the indicator electrode (when an appropriate potential is chosen for the latter). In our case in order to assess the changes which occur in the composition of the solution during titration, we took current — voltage curves (polarograms) during titration. The polarograms obtained are shown in Fig. 4; curves 1 and 2 were taken shortly before the end point (when the solution had been titrated to the extent of about 90%); at a potential of +0.7 v, on these curves, one of which corresponds to a solution containing sulfuric and hydrochloric acids, while the second corresponds to a solution of hydrochloric acid and Z.R. mixture, there is observed only an insignificant current corresponding to the incipient reduction of Fe^{3+}, formed from Fe^{2+} during oxidation of the latter. Curves 1a and 2a correspond to curves 1 and 2, but taken after the end point, with 0.2 ml of 0.05 N permanganate solution present in excess. In the case of curve 1a, the solution obtained after the end point acquires a yellow color (Fe^{3+} in a hydrochloric acid medium), the odor of chlorine is detectable, and the shape of the polarogram indicates reduction of chloride, followed by reduction of Fe^{3+} (at a potential of +0.7 v only reduction of chloride occurs). Curve 1a almost coincides with curve 3 on the same figure, Fig. 4, which was taken specially for comparison in a sulfuric acid solution of chlorine water containing Fe^{3+}. In the case of curve 2a, the solution has a cherry-red color, while the shape of the curve coincides with the polarogram for permanganate in a supporting electrolyte of hydrochloric acid and Z.R. mixture shown in Fig. 3 (curve 2).

Titration curves of different shape can be obtained by choosing another potential for the indicator electrode.

A comparison of our results with published data leads to the following conclusions: the first titration stage – from the beginning of titration to the end point – proceeds in the same way both in a supporting electrolyte of sulfuric acid and in a supporting electrolyte of Z.R. mixture, and consists in the oxidation of Fe^{3+} with permanganate. Comparison of the values of the normal potentials of the systems MnO_4^-/Mn^{2+} and Fe^{3+}/Fe^{2+} (+1.54 and +0.79 v) shows that from an energy point of view this process is quite possible and that there is no need to postulate formation of intermediate oxides of higher valence. In a supporting electrolyte of hydrochloric acid, during the first stage of the titration, oxidation of Fe^{2+} by permanganate also occurs, while after the end point oxidation of chloride ions by excess permanganate occurs; during the first stage of titration, in parallel with oxidation of iron, there also occurs, but only to a very small extent as a side reaction, formation of free chlorine, which gradually increases as the end point is approached. Proof of the fact that this process is a side reaction is that the titration end point is very sharp in this case too, and coincides with the end point in the absence of hydrochloric acid. Presumably, oxidation of chloide ions during the first stage of the titration is effected by Mn^{3+} ions formed by the oxidation of Fe^{2+} by permanganate, while after the end point oxidation is effected directly by the permanganate. When Z.R. mixture is present, i.e., in the presence of a large excess of Mn^{2+} ions, a reaction occurs between the latter and permanganate, and not between the chloride ions and permanganate. This reaction leads to the formation of Mn^{3+}, the stability of which in the given instance is ensured by the presence of phosphoric acid. From an energy point of view, the reaction between permanganate and Mn^{2+} ions present in large excess, and which, accordingly lower the potential of the system Mn^{3+}/Mn^{2+}, is more efficient than the oxidation of the chloride ions, since the potential of the system Mn^{3+}/Mn^{2+} is less positive than the potential of the system $Cl_2/2Cl^-$, particularly in the presence of phosphate which complexes the Mn^{3+} ion.

SUMMARY

An amperometric method has been used for studying titration of divalent iron with permanganate in sulfuric, and hydrochloric acid solutions and in hydrochloric acid solutions containing Zimmerman-Reinhardt mixture.

It has been shown that in all three supporting electrolytes, before the end point is reached, titration of iron with permanganate consists in the direct oxidation of Fe^{2+} ions by permanganate.

Normal visual titration is impossible in a hydrochloric acid medium because after the end point the chloride ions start to react with permanganate and lead to decolorization of the solution.

Addition of Zimmerman-Reinhardt mixture eliminates this phenomenon, since in this case the permanganate oxidizes the Mn^{2+} ions and not the Cl^- ions; the Mn^{3+} formed which is complexed by phosphate is responsible for the stable cherry-red color of the solution, this color serving as an indicator during visual titration.

It has been shown that by using an amperometric method it is possible to titrate iron with permanganate in a hydrochloric acid medium without adding Zimmerman-Reinhardt mixture.

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THE SOLUBILITY PRODUCT OF ETHYLENEDIAMINETETRACETIC ACID

G. S. Tereshin and I. V. Tananaev

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences
of the USSR, Moscow

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The solubility of ethylenediaminetetracetic acid (EDTA)* has been determined by a number of research workers [1-5]. The solubility product has, however, not hitherto been calculated. Using published data on the solubility of EDTA we have calculated $Z_{\text{sol. EDTA}}$.

Klygin, Smirnova, and Nikol'skaya [4] have established the relationship between the solubility of EDTA and pH at 25°. They concluded that a cation of the ammonium type H_6Y^{2+} exists, and calculated its dissociation constant. They did not take into account, however, the possibility of successive addition of protons to the EDTA molecule, and the presence of its dissociation product (H_3Y^-). We have taken these factors into account in our calculations. We used the data on the solubility of EDTA in hydrochloric acid solutions for our calculations ([4] table).

At pH < 2, the concentration of H_2Y^{2-}, HY^{3-}, and Y^{4-} is negligible and can be ignored. One must, however, take into account possible addition compounds formed by addition of protons to the EDTA molecule. Tillotson and Stavely [6] who calculated the dissociation constant of the ion H_5Y^+, were the first to point out the existence of such cations in solution. They also assumed formation of a H_6Y^{2+} ion, but were unable to prove this experimentally. Klygin [4], as indicated above, denies the existence of the H_5Y^+ ion, and states that two hydrogen ions add on simultaneously to the amino groups in EDTA. Palei and Udal'tsova [5] also postulate formation of the H_6Y^{2+} ion in solution. In addition, these authors isolated from strongly acid (3 N HCl) solutions of EDTA, a sparingly soluble compound $[H_6Y]Cl_2$ or $H_4Y \cdot 2HCl$ (and the analogous sulfate of EDTA). We did not take the possibility of the formation of such compounds into account in our calculations, since we used solubility values obtained at fairly high pH values (> 0.8).

Taking what has been said above into account, the solubility of EDTA is equal to

$$S = \sum_{i=3}^{6} [H_iY^{i-4}]. \tag{1}$$

The concentrations of the individual ionic (and molecular) forms of EDTA are equal to:

$$\left.\begin{aligned} [H_3Y^-] &= \frac{[H^+]^3\,[Y^{4-}]}{k_2k_3k_4}, \\ [H_4Y^0] &= \frac{[H^+]^4\,[Y^{4-}]}{k_1k_2k_3k_4}, \\ [H_5Y^+] &= \frac{[H^+]^5\,[Y^{4-}]}{k_0k_1k_2k_3k_4}, \\ [H_6Y^{2+}] &= \frac{[H^+]^6\,[Y^{4-}]}{k_{00}k_0k_1k_2k_3k_4}, \end{aligned}\right\} \tag{2}$$

where k_1, k_2, k_3, and k_4 are the respective dissociation constants of EDTA and

$$\left.\begin{aligned} k_0 &= \frac{[H^+]\,[H_4Y]}{[H_5Y^+]}, \\ k_{00} &= \frac{[H^+]\,[H_5Y^+]}{[H_6Y^{2+}]}. \end{aligned}\right\} \tag{3}$$

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* Designated as H_4Y.

The solubility of EDTA is determined by the formula

$$L_p = [H^+]^4 [Y^{4-}]. \tag{4}$$

From relations (1), (2), and (4) by algebraic transformation we obtain:

$$S \cdot [H^+] = \frac{L_p}{k_2k_3k_4} + \frac{L_p}{k_1k_2k_3k_4} \cdot [H^+] + \frac{L_p}{k_0k_1k_2k_3k_4} \cdot [H^+]^2 + \frac{L_p}{k_{00}k_0k_1k_2k_3k_4} \cdot [H^+]^3. \tag{5}$$

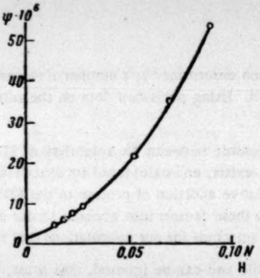

Fig. 1. Graphical determination of B_0.

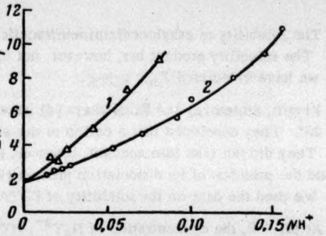

Fig. 2. Graphical determination of B_1. 1) $\Delta\psi$ per ΔH; 2) ψ_1.

Designating $[H^+]$ by H and $S \cdot [H^+]$ by ψ and introducing the appropriate designations for the coefficients in front of $[H^+]$, equation (5) can be represented in the form

$$\psi = B_0 + B_1 \cdot H + B_2 \cdot H^2 + B_3 \cdot H^3. \tag{6}$$

We determined the coefficients of this equation graphically. Figure 1 shows the curve relating ψ and H. By extrapolating the curve to zero hydrogen ion concentration we obtained the value of B_0:

$$H \to 0, \ \psi \to B_0 = 1{,}8 \cdot 10^{-6}.$$

We used the values of the dissociation constants of EDTA determined by Schwarzenbach at 20° [7] for calculating the value of L_{sol}. Errors arising from temperature differences were not taken into account in view of the large errors arising from the inconstancy of the ionic strength in the experiments used.

$$L_{sol} = k_2k_3k_4 \cdot B_0 = 1{,}45 \cdot 10^{-25}.$$

From (6) we find that

$$\frac{d\psi}{dH} = B_1 + 2B_2 \cdot H + 3B_2 \cdot H^2. \tag{7}$$

The curve $\Delta\psi / \Delta H - H$ is shown in Fig. 2 (curve 1), where H designates the mean point of the range for which the slope $\Delta\psi/\Delta H$ is calculated.

$$H \to 0, \ \frac{\Delta\psi}{\Delta H} \to B_1 = 1{,}8 \cdot 10^{-4}.$$

We also determined B_1 by extrapolating the function

$$\psi_1 = \frac{\psi - B_0}{H} = B_1 + B_2 \cdot H + B_3 \cdot H^2. \tag{8}$$

to H = O (Fig. 2, curve 2): $\psi_1 \to B_1 = 1.8 \cdot 10^{-4}$.

From which

$$L_{sol} = k_1 k_2 k_3 k_4 \cdot B_1 = 1{,}45 \cdot 10^{-26}.$$

The same value of L_{sol} was obtained as that derived from B_0. Next the following function was plotted (Fig. 3)

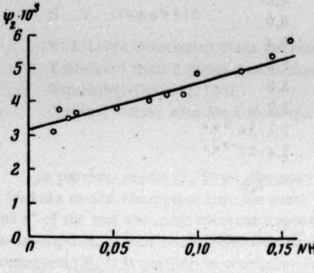

Fig. 3. Graphical determination of B_2 and B_3.

$$\psi_2 = \frac{\psi_1 - B_1}{H} = B_2 + B_3 \cdot H. \tag{9}$$

$$H \to 0, \ \psi_2 \to B_2 = 3{,}2 \cdot 10^{-3}.$$

The fact that B_2 differs from zero indicates the existence of a cation of the ammonium type H_5Y^+. We calculated the value of k_0 from the value found for B_2:

$$k_0 = \frac{L_{sol}}{k_1 k_2 k_3 k_4 B_2} = 5{,}6 \cdot 10^{-2}, \ pk_0 = 1{,}25.$$

Tillotson and Stavely [5] found $pk_0 = 1.55 \pm 0.13$ for 20° at $\mu = 0.1$.

It follows from (9) that:

$$\frac{\Delta \psi_2}{\Delta H} = B_3. \tag{10}$$

The slope of the straight line in Fig. 3 differs from zero. Accordingly, the cation H_6Y^{2+} exists. The slope was found to be equal to $B_3 = 1.4 \cdot 10^{-2}$. From which

$$k_{00} = \frac{L_{sol}}{k_0 k_1 k_2 k_3 k_4 B_3} = 2{,}2 \cdot 10^{-1}, \ pk_{00} = 0{,}66.$$

The total dissociation constant of a cation of the ammonium type H_6Y^{2+} is given by

$$K = \frac{]H_+]^2 [H_4Y]}{[H_6Y^{2+}]} = k_0 k_{00} = 1{,}23 \cdot 10^{-}.$$

This value was found to be in agreement with that calculated by Klygin, Smirnova, and Nikol'skaya [4]. These authors, however, did not take into account the existence of the H_5Y^+ ion([4], equation (4)]. Obviously, the concentration of undissociated molecules which they calculated $[H_4Y] = 3.56 \cdot 10^{-4}$, was greater than the solubility of EDTA for a series of pH values.

It is interesting to compare the calculated value of $L_{sol.\,EDTA}$ with that calculated on the basis of the results of Mechelynck and Schietakatte [1]. These results, presumably, relate to room temperature. The solubility of EDTA was determined over the pH range 1.13-7.32.

In our calculations we took into account all possible fragments of EDTA, apart from Y^{4-}. An equation similar to equation (5) was derived. $L_{sol.\,EDTA}$ was calculated for each pH value, by means of this equation.

It is clear from the table that the calculated values of L_{sol} are constant over the pH range 1.13-4.67. At pH 6.12 and 7.32, obviously low values of L_{sol} were obtained (three and six orders lower respectively). This apparently indicates changes in the composition of the precipitate.

The mean geometrical value [8] of the calculated values of L_{sol} is equal to $4.0 \cdot 10^{-26}$. This value is less than the value obtained for L_{sol} on using the results of Klygin et al. The deviations are obviously the result of difference in temperature.

It is impossible to calculate the values of $L_{sol.\,EDTA}$ on the basis of the results given by the Japanese workers [2, 3] and by Palei and Udal'tsova [5] since these authors did not measure the pH of the solution.

Calculations of $L_{sol.\,EDTA}$ on the Basis of Mechelynck and Schietakatte's Results

pH	S, M	$L_{sol} \cdot 10^{26}$
1.13	$3.07 \cdot 10^{-4}$	6.5*
1.97	$1.73 \cdot 10^{-4}$	5.6*
2.86	$7.18 \cdot 10^{-4}$	3.0
3.31	$3.33 \cdot 10^{-3}$	2.4
3.80	$3.90 \cdot 10^{-2}$	3.4
4.11	$3.46 \cdot 10^{-1}$	5.5
4.67	1.87	3.2
6.12	1.81	$2.1 \cdot 10^{-3}$**
7.32	2.42	$1.4 \cdot 10^{-6}$**
Mean		4.0

* $pk_0 = 1.55$ was used in the calculations [7]. The presence of H_6Y^{2+} was not taken into account.

** Not taken into account when the mean value was determined.

SUMMARY

Using published data on the solubility of ethylenediaminetetracetic acid, the value of the solubility product of this acid has been determined. At 25° $L_{sol} = 1.45 \cdot 10^{-25}$.

Calculations have demonstrated the existence of two products which are formed by the successive addition of protons to the EDTA molecule, they are H_5Y^+ and H_6Y^{2+}. Their dissociation constants have been calculated (at 25°); they were found to be equal to $pk_0 = 1.25$ and $pk_{00} = 0.66$ respectively.

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A METHOD FOR CORRECTING THE RELATIVE INTENSITY OF ANALYTICAL PAIRS OF LINES IN AN ARC DISCHARGE

G. V. Ovechkin

V. I. Lenin Belorussian State University, Minsk

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In previous papers [1, 2] we discussed the reasons for the displacement of the calibration curve, and arrived at a formula on the assumption that the terms in the equation, which include the degree of ionization of the atoms x and x' of the test and main element respectively, act in opposite directions for atomic and ionic pairs of lines. Such an assumption, as will become evident from what follows, proved to be erroneous. Using Sach's formula and Unzold's nomogram [3], it is possible to determine approximately the relationship between the values of log (x_n/x'_n), log $(1-x_n/1-x'_n)$ and the plasma temperature for tin which has an ionization energy of ϵ = 7.33 ev (impurity) and copper with ϵ' = 7.72 ev (the main element), which are shown in Fig. 1. When copper is the impurity element and tin the main element, then the curves for the values of log (x_n/x'_n) and log $(1-x_n/1-x'_n)$ change places like a mirror image relative to the abscissa. The extent of the two-fold ionization of the atoms must be taken into account at the temperature of the plasma spark, and this was not done in the given instance.

As Fig. 1 shows, the relative content of tin and copper ions increases with decreasing plasma temperature. At the same time the relative content of their neutral atoms also increases. Accordingly, there is no basis for changing the sign in the equation before the term [1]. It is also clear from the diagram that at low temperatures the value of

$$\lg\frac{1-x_n}{1-x'_n}-\lg\frac{1-x_0}{1-x'_0} \qquad (1)$$

is less than the experimental error $\Delta S = \pm 0.02$. For example, on dropping the plasma temperature from 6000 to 5000° in the case of the elements Ca—Cu this difference is 0.008, while on dropping the temperature from 7000 to 6000° for Cr—Cu the difference is 0.016. Accordingly, the difference (1) can be excluded from consideration during a discussion of the results obtained by means of an arc discharge in the case of nonalkali metals. In such a case, the formulas for the fractional displacements of the curves assume the following forms:

1) Because of changes in the value of the exponential function

$$\frac{1}{n}-\frac{1}{T_0}=\frac{k\,(\delta S'_n-\delta S''_n)}{0{,}43\cdot\gamma\,(|\,\Delta E'+\Delta E'')}. \qquad (2)$$

2) Because of changes in the relative content of the ions

$$\lg\frac{x_n}{x'_n}-\lg\frac{x_0}{x'_0}=\frac{\delta S'''_n-\delta S'_n}{\gamma}+\frac{(\Delta E''-\Delta E^a)\,(\Delta S'_n-\delta S''_n}{\gamma\,(|\,\Delta E'\,|+\Delta E'')}. \qquad (3)$$

3) As a result of changes in the relative rate of evaporation of the elements being compared and their diffusion in the plasma

$$\lg\frac{d_n}{\beta_n}-\lg\frac{d_0}{\beta_0}=\frac{\delta S'_n}{\gamma}+\frac{\Delta E^a\,(\delta S'_n-\delta S''_n)}{\gamma\,(\Delta E'+\Delta E'')} \qquad (4)$$

where $\delta S_n'''$, $\delta S_n'$ and $\delta S_n''$ are the values of the total displacement of the curve respectively for the ionic pairs of lines, the atomic pairs of lines with $\Delta E' < 0$, and the atomic pairs of lines with $\Delta E'' > 0$, on dropping the plasma temperature from T_0 to T_n (for details see [1, 2]); ΔE is the difference in the excitation energy of the corresponding pairs of lines. The fractions of the displacement which can be attributed to each cause have been established experimentally, and confirm the correctness of the theoretical conclusions.

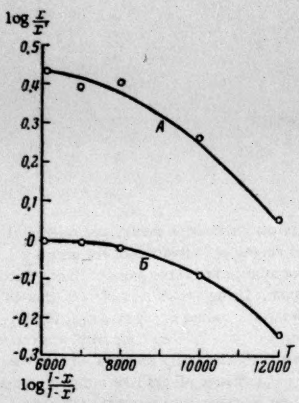

Fig. 1. Curves for the relationships between relative content of A) Ions, log (x_n/x'_n) and B) neutral atoms Sn—Cu, log $(1-x_n/1-x'_n)$ and plasma temperature.

The extents to which the curve is displaced as a result of the action of the corresponding factor were established from the experimentally established total displacement of the curve for three pairs of lines at a known concentration of the test element in standards. In practice, as a rule, the reverse is met — determination of the concentration of an element on the basis of the relative intensity of the analytical pair of lines emitted, the solution of which is set forth in the present article. Such a problem can be resolved with a reasonable accuracy by using calibration curves, on the condition that one takes into account the change in the relative intensity of the radiation of the analytical pair of lines arising from a possible change in the degree of ionization of the atoms of the element being compared, in their relative evaporation rates, and in the value of the exponential function caused by changes in the discharge conditions.

As soon as formulas (2-4) for calculating the fractional displacements of the curve have been established theoretically, and their correctness has been confirmed experimentally, the problem posed can be partially solved in the following manner, in the case of the determination of nonalkali metals in an arc discharge. We represent the calibration curves of the corresponding pairs of line one above the other, preserving their experimentally determined slopes, the values of their displacement, and the arrangement of the points along the abscissa as shown in Fig. 2. The arrangement of the points along the ordinate is arbitrary. The differences in the blackening density of the analytical pairs of lines are plotted along the ordinate, while the logarithm of the relative concentration of the test element is plotted along the abscissa.

The straight lines A'' and A' represent calibration curves for the atomic pairs of lines of tin and copper respectively with positive and negative ΔE values. They were obtained in the absence of an oxide film and under conditions of weak reabsorption of the spectral lines. The true path of the curve for the ionic pair of lines with a negative value of $\Delta E'''$ is shown by the dot-dash line. Its slope is different from the slopes of the curves for the atomic pairs of lines. The angle between them is ω. To keep the whole thing in perspective we depict this curve A''' in parallel with curves A'' and A'. The continuous straight lines A_0 were obtained using binary standards, while the dotted lines A_n were obtained using standards containing 10% sodium. We shall denote the values of the displacement of the curves for the atomic pairs of lines with a positive value of $\Delta E''$ by $A_0''A_n'' = B_0''B_n'' = \delta S_n''/\gamma$, for the atomic pair of lines with a negative value of $\Delta E'$ by $A_0'A_n' = B_0'B_n' = \delta S_n'/\gamma$, and for the ionic pair of lines by $A_0'''A_n''' = C_0'''E''' = \delta S_n'''/\gamma$. The points A_0'', A_0', and A_0''' are the values of the relative intensity of the corresponding analytical pairs of lines for a certain tin concentration. They lie on the curves constructed on the basis of standards of a binary composition. Addition of 10% sodium to the standards leads to an increase in the relative intensity of the pairs of lines, despite the fact that the relative content of tin and copper remains the same.

The relative intensities of the analytical pairs of lines for samples containing sodium are denoted by A_n'', A_n' and A_n'''. They lie on the curves constructed on the basis of standards containing 10% sodium. Were these values of the relative intensity of the pairs of lines plotted on the curves obtained with binary standards, then points B_0'', B_0', and D or B_0''' would correspond to them. Determination of the concentration of tin in a sample on the basis of these points would lead to different results for different pairs of lines.

As Fig. 2 shows, the concentration of the elements found in a sample proves to have different values and is high, and it becomes higher on switching from the curve for the atomic pair of lines with $\Delta E'' > 0$ to the curve for the atomic pair of lines with $\Delta E' < 0$, and to the curve for the ionic pair of lines. It is also clear from the diagram that the apparent increase in concentration of the element being determined, when it is determined by the curves for different pairs of lines, points to an increase in the relative intensity of the emission of these pairs of lines or to a displacement of their calibration curves upwards on adding sodium to a sample.

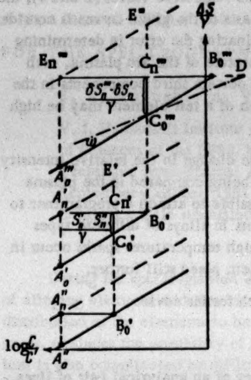

Fig. 2. Schematic diagram of the curves relating the relative intensity of line pairs and the concentration of tin relative to copper content: A'' = Sn I 2429 – Cu I 2492 with $\Delta E'' > 0$. A' – Sn I 2429 – Cu I 2766 with $\Delta E' < 0$ and A''' – Sn II 2246 – Cu II 2242 with $\Delta E''' < 0$. The continuous lines were obtained using binary standards; the dotted lines were obtained using standards containing 10% sodium.

In the case under consideration the relative intensity of the spectral lines increases on adding sodium to a sample, both as a result of an increase in the content of the tin being determined (α) relative to copper (β) the main element in the plasma, and as a result of an increase in the relative content of their ions. Addition of sodium to a tin-chromium sample, made from the respective chlorides, leads, on the other hand to a decrease in the content of the test tin (α) relative to the main element chromium (β) in the plasma, and leads to a decrease in the relative content of their ions, as a result of which the relative intensity of the pairs of lines decreases. In such a case the concentration, determined on the basis of the relative intensities of the lines, and on the basis of the curves of binary standards, proved to be low. Accordingly, it is possible, to establish accurately, on the basis of the increase or decrease in the concentration of an element, which is observed on switching from the curves of one pair of atomic lines to the curve for another pair of atomic or ionic lines, whether the relative intensity of the corresponding pairs of lines increases or decreases as the result of changes in the content of the ternary components in the sample, or in the discharge conditions. If it is possible thereby to determine the amount by which the relative intensity of the analytical pairs of lines changes as a result of third component effects, or as a result of changes in the discharge conditions, it should be possible to develop a method for determining the contents of elements in any samples on the basis of binary standards.

In order to determine the amount by which the relative intensity of the analytical pairs of lines changes as the result of these respective reasons, lines are drawn from points B_0'', B_0', and B_0''' parallel to the ordinate and abscissa. As a result, a series of right angled triangles is obtained. Let us compare triangles $A_n''B_n'B_0''$ and $A_n'E'B_n'$. On comparing them it is evident that the angles $\angle B_0''A_n''B_n'' = \angle B_n'A_n'E'$, $\angle A_n''B_n''B_0'' = \angle A_n'DB_n'$, $\angle B_n''B_0''A_n'' = \angle D'B_n'A_n'$ and sides $A_n''B_0'' = A_n'B_n'$, $A_n''B_n'' = A_n'D'$ are equal. Since all the corresponding angles and the two sides of the triangles compared are equal, it follows that their third sides are also equal, viz: $C_n'C' = B_0''D_n'' = \delta S_n''/\gamma$. Consequently

$$B_0'B_n' = \frac{\delta S_n' - \delta S_n''}{\gamma}. \tag{5}$$

This accordingly gives a method for determining the value of $(\delta S_n' - \delta S_n''/\gamma)$ on the basis of the curves for binary standards. Having experimentally determined the numerical value of the relation (5), it is possible by means of formula (2) to find the value by which the relative intensity of the respective pairs of lines changes when the values of the exponential function change as a result of a decrease or an increase in the plasma temperature.

The triangles $A_n'B_n'B_0'$ and $A_n'''D'''B_n'''$ are compared next. It is clear from the diagram that their corresponding angles and two sides are equal, so that their third sides are also equal, thus: $D'''B_n''' = B_n'B_0' = \delta S_n'/\gamma$. We then obtain

$$B_n'''B_0''' = \frac{\delta S_n''' - \delta S_n'}{\gamma}. \tag{6}$$

In this way a method is also found for determining the value of $\delta S_n''' - \delta S_n'$. If the smaller slope of the curves for the ionic pairs of lines is taken into account, then

$$B_n'''B_0''' = \frac{\delta S_n''' - \delta S_n'}{\gamma \cdot \cos\omega}. \tag{7}$$

Knowing the numerical values of relationships (5) and (7), it is possible, by using formula (3), to calculate the value by which the relative intensity of the ionic pairs of lines alters as a result of changes in the relative content of the ions of the elements being compared, following upon a decrease or increase in the plasma temperature.

After correcting the relative intensity of the corresponding pairs of lines by the respective values (2 and 3), the accuracy with which the concentration of the elements can be determined on the basis of the given curves is considerably increased. In this way it has been found possible to solve the problem of eliminating the error in determining the concentration of a test element which arises as a result of changes in the temperature of the arc plasma, such temperature changes being possible when the discharge conditions or the content of certain third components in the sample alter. As Semenova has shown [4] the error in determining the concentration of a test element may be high because of such changes.

Unfortunately, the question of how it is possible to determine the extent of the change in the relative intensity of the pairs of lines following upon changes in the relative content of the elements being compared in the plasma (4), still remains unsolved. If this problem could be solved as well, it should be possible to attach a programmer to the multichannel DFS-10 apparatus, and determine the concentration of the elements in alloys of different types automatically on the basis of one calibration curve. As is evident from Fig. 1, at high temperatures sparks occur in the plasma, and the value (1) is higher. This fact complicates solution of the problem posed still further.

In conclusion I should like to express my warmest thanks to M. A. El'yashevich for his advice.

SUMMARY

A method is given for calculating the change in the relative radiation intensity of an analytical pair of lines, caused by a decrease or an increase in the arc plasma temperature following upon changes in the discharge conditions. The values $(\sigma S'_n - \sigma S''_n/\gamma)$ (5) and $(\sigma S''_n - \sigma S'_n/\gamma)$ (6) are determined from the calibration curves for the two pairs of atomic lines and one pair of ion lines. Subsequently, it is possible, by means of formulas (2) and (3), to determine the values of the change in the relative intensity of the pair of lines following upon changes in the value of the exponential function and in the degree of atom ionization.

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EXCITATION CONDITIONS OF THE SPECTRA OF ELEMENTS IN A PLASMA GENERATOR AND THE APPLICATION OF THE LATTER FOR THE SPECTROGRAPHIC ANALYSIS OF TITANIUM ALLOYS

É. E. Vainshtein, V. V. Korolev, and E. N. Savinova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy
of Sciences of the USSR, Moscow

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During the spectrographic determination of impurities in titanium metal or during the control of the content of alloying elements added to titanium alloys, it is always necessary to take into account the possibility of uneven distribution of the elements to be determined in the test material. This gives rise to additional errors, and, in some cases, excludes the possibility of using an arc or spark excitation source. During analysis of titanium alloys the problem is also complicated by difficulties associated with the preparation of standard samples. Accordingly, in most current techniques [1-3], determination of impurities in titanium and in its alloys is carried out after converting titanium into its dioxide, the latter being then analyzed spectrographically by excitation in an arc. A much more radical approach for overcoming such difficulties is to resort to analyzing solutions, which, in the case of titanium alloys can be realized with exceptional ease and simplicity. Several such methods have been described [3-6], in which the metal is brought into solution, and the latter subsequently analyzed with a porous or rotating electrode with excitation of the spectrum in a spark.

Great possibilities have been opened up thanks to the introduction into spectrographic practice [7, 8] of a new excitation source, the so-called plasma generator, which allows, as experience has shown [7, 9], the accuracy and reliability of the spectrographic determination of elements in solution to be increased considerably.

The present article is devoted to a technique which we have developed for the analysis of titanium alloys by means of a plasma generator. Results of a study of certain characteristics of the new excitation source are also included.

Study of the excitation conditions of the spectra of various elements in the source. A plasma generator adapted for the analysis of solutions, and whose design has already been described earlier [9] was used in the work.

An attempt was made during a series of systematic experiments to establish the way in which the blackening of the analytical lines of various elements changes along the length of the source stream, and to study the effect of certain factors, which influence the excitation conditions of the atoms of the elements in the plasma, on the form and spatial distribution of these curves. Of these factors we first examined the ionization potential of the elements and the excitation energy of their emission lines, the source temperature, and the effect of cations and anions. In addition, of no little interest was an examination of the effect on the excitation conditions of the elements, of the addition of organic materials to the test solutions, in paricular addition of ethanol, the presence of which, as our preliminary observations have shown [9], is reflected in the radiation intensity of the line of an element in a plasma stream.

The results of these experiments are shown in Figs. 1-6. An examination of these leads to the following conclusions:

1) A decisive effect on the shape and the position of the maxima on the curves relating line blackening of various elements to the distance from the base of the plasma generator stream (Fig. 1) is shown by the value of the excitation energy of these lines. The ionization potential of the element, has, in practice almost no significance. With decreasing excitation energy of the emission lines, there is observed, as a rule, a widening in the maximum of the curves considered, while its position is shifted along the length of the stream away from the base. This

deformation in the shape of the curves can be particularly clearly followed in the case of the lines of the alkali elements (Fig. 2.

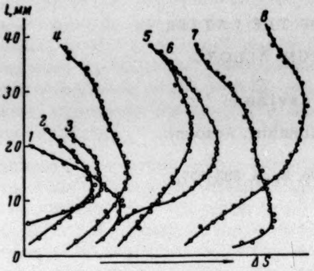

Fig. 1. Change in line blackening (ΔS) of various elements (compared with the blackening of the spectrogram background) along the length of the plasma generator stream. *l* is the distance in mm from the base of the stream. 1) For the line Fe II 2410.5 (5.25 ev); 2) Fe I 3019 (5.06 ev); 3) Cr I 3017.6 (5.1 ev); 4) Al I 2652.5 (4.66 ev); 5) Ti II 3234.5 (3.9 ev); 6) V I 3185.4 (4 ev); 7) Zn I 3345.0 (7.78 ev); 8) Cr I 4254.4 (2.9 ev). The excitation potentials of the lines are given in brackets. The relative position of the curves along the abscissa is arbitrary.

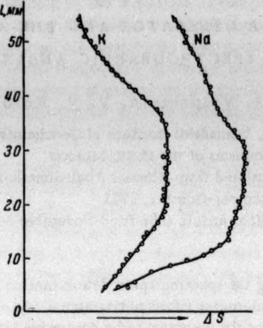

Fig. 2. Change in blackening of the lines K I 3446.7 (3.60 ev) and Na I 3302.3 A (3.75 ev) along the plasma generator stream. The relative position of the curves along the abscissa is arbitrary.

The position of the maximum and the shape of the curves considered are very close (e.g., curves 2 and 3, or 5 and 6 in Fig. 1) in the case of the lines of various elements with similar excitation potentials. On the other hand, when there is an appreciable difference in the values of the excitation potentials of the lines, even of the same element (curves 3 and 8 in Fig. 1), the shape of these curves and the position along the plasma stream corresponding to the blackening maximum of the respective lines can differ from each other to a very considerable extent. This fact must be borne in mind when choosing the analytical lines of the elements, and the optimum conditions for carrying out analyses of various objects. On the one hand, the effect indicated sets certain limitations and can, for example, sometimes complicate the choice of reference lines which are suitable under other relationships, while on the other hand, as a result of the possibility of a spatial separation of the maxima of successfully chosen analytical lines of various elements along the plasma stream, it opens up the possibility of artificially increasing the line intensity of certain elements at the expense of the weakening of others by correct choice of the operating part of the plasma stream.

2) Anions do not affect the character of the distribution of line intensity of the elements in a plasma generator stream (Fig. 4).

Cations of other elements present in solution, judging from available data (Fig. 3), may sometimes give rise to a small (and seldom realized from a practical point of view) shift in the original curves. This question, however, deserves a wider and more systematic study.

3) In order to have an idea of the nature of the change in the excitation conditions of the lines of the elements on moving along the plasma generator stream, a study was made of the relationship between the relative intensity of the spark and arc lines of iron (or for simplicity ΔS) and the distance to the base of the stream (*l*), in which various sections of the radiating plasma were projected on the spectrograph slit. It was established during the course of this study (Fig. 5) that there is a linear decrease in the difference in the blackening of the lines of the fixed pair used, indicating thereby an uniform decrease in the source temperature as one moves along the stream from its base to its periphery.

Addition of ethanol (50%) to the solution does not destroy the general features of the relationship between the temperature of a corresponding zone of the source plasma and its position in the stream (curve w, Fig. 5), but leads to an experimentally fixed decrease in the source temperature as a whole. In accordance with this, addition of alcohol also has an effect on the position of the maximum and on the shape of the curves relating blackening of the analytical lines of test elements to distance of the various zones of the stream from the base (Fig. 6). As one might expect, in view of what has been said above, the presence of alcohol in solution leads to an expansion of the original curves, and to the displacement of their maxima toward the base of the stream. A certain increase in the intensity of the analytical lines of the elements is also observed, the magnitude of the increase being dependent on the values of the excitation potentials of the elements; on an average it usually amounts to 1.5-2 times.

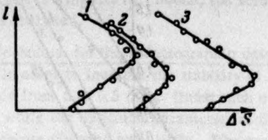

Fig. 3. Effect of foreign cations present in the plasma on the nature of the relationship between the intensity of the line Fe I 2719.02 A and the distance to the base of the plasma stream. 1) In absence of other cations in the plasma (iron as $FeSO_4$); 2) $FeSO_4$ to which large amounts of $KHSO_4$ have been added; 3) $FeSO_4$ to which large amounts of $ZnSO_4$ have been added. The mutual position of the curves along the abscissa is arbitrary.

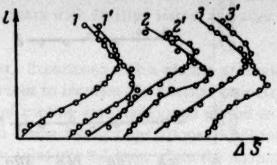

Fig. 4. The relationship between the character of the distribution of the blackening of iron lines and the presence of various anions in the plasma. 1) SO_4^{2-}; 2) Cl^-; 3) NO_3^-. The ordinary figures relate to the line Fe II 2598.4 while the dashed figure relate to Fe I 2719.02. The mutual position of the curves along the abscissa is arbitrary.

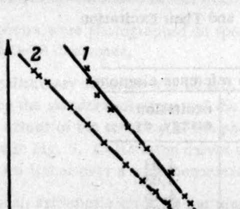

Fig. 5. The change in the difference in blackening of the fixed pair Fe II 2598.4 and Fe I 2719.02 (ΔS) along the length (*l*) of the plasma stream. 1) During excitation of the element from pure aqueous solutions; 2) on addition of a solution containing 50% ethanol.

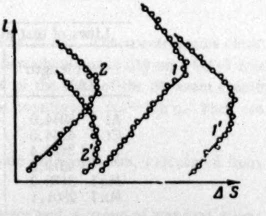

Fig. 6. Effect of addition of ethanol (50%) on the distribution of blackening of the iron lines Fe I 3020.6 (1) and Fe II 2392.0 (2) along the length of the plasma stream. The ordinary figures refer to solutions free from ethanol; the dashed figures refer to solutions which ethanol has been added. The relative position of the curves along the abscissa is arbitrary.

Technique for analyzing alloys. The technique described below can be used for the quantitative determination, in practice, of all the alloying elements usually added to titanium alloys (Al, Cr, Mo. Fe, Si, V, Mn, Sn). Nevertheless, in the present article the possibilities of the technique are described only with respect to the determination of five of these additives, the so-called α- and β-stabilizors – Al, Cr, Mo, V, and Mn – the content of which in various alloys can be varied over a wide range of 0.1 to 10%.

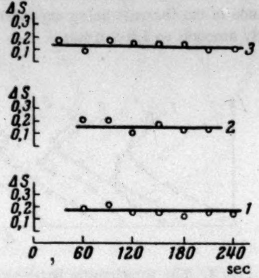

Fig. 7. The degree of constancy of the blackening of the analytical lines of various elements (ΔS) during their excitation from solution in a plasma stream. 1) For the lines Al I 3944.0; 2) Cr I 4254.3; 3) Fe I 3019. The blackening level of the line is arbitrary.

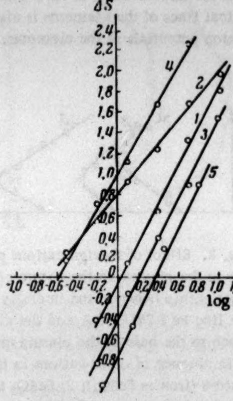

Fig. 8. Calibration curves for the determination of Al (1) Gr (2); Mo (3); Mn (4); and V (5) in titanium alloys.

TABLE 1. Analytical Lines of the Elements and Their Excitation Potentials

Lines of test elements		Lines of the reference element	
wavelength (A)	excitation energy, ev	wavelength (A)	excitation energy, ev
Al I 3944,0	3,14	Co I 3995,3	4,03
Cr I 4254,3	2,91	Co I 3995,3	4,03
V I { 3183,4	3,91	Co I 3412,0	4,15
V I { 4379,2	3,13	Co I 3995,3	4,03
Mo I 3170,3	3,91	Co I 3412,0	4,15
Mn I 2801,1	—	Co I 3412,0	4,15

TABLE 2. Results of Chemical (Ch) and Spectrographic (S) Analysis of Standard Alloys

Standard No.	Mo		Cr		Al		Mn	
	Ch	S	Ch	S	Ch	S	Ch	S
11	2,50	2,52	4,16	4,21	2,90	2,92	3,15	3,10
12	—	—	0,92	0,89	3,83	3,67	0,72	0,68
13	—	—	—	—	5,03	5,13	—	—
14	0,74	0,70	1,60	1,59	5,31	5,20	1,10	1,07
17	1,50	1,66	2,35	2,40	7,02	6,90	0,79	0,78

a) Preparation of standard solutions and preparation of samples for analysis. Standard solutions are prepared by mixing calculated amounts of solutions of the chlorides of the test elements and of the base element (titanium), with addition of 5 ml of a cobalt salt solution (10 mg Co/ml), cobalt being used as the reference element. A standard with the maximum content of the test components is first prepared, and the other standards prepared from this by appropriate dilution with a solution of titanium salt containing 1% Ti.

A 0.5 g aliquot of the turnings of the test alloy is placed in a chemical beaker, 20 ml of chemically pure concentrated hydrochloric acid which has been checked beforehand for the absence of the elements to be determined is added, the beaker is covered with a watch glass and the contents of the beaker are heated on a sand bath until the alloy has dissolved. As the solution is evaporated HCl is added to it in small portions. When dissolution is complete, the dark-violet colored solution of titanium trichloride is oxidized with chemically pure, concentrated nitric acid, the latter being added dropwise. The solution obtained is transferred to a 50 ml standard flask and 5 ml of a solution of a cobalt salt (10 mg Co/ml) added, the solution is made up to the mark with distilled water, and after thorough mixing it is analyzed.

b) Technique for the spectrographic determination of elements. Experience with a plasma generator [9] has shown that in order to increase the stability of the stream, it is expedient to increase the internal diameter of the outlet nozzle from 5 to 6.5 mm. Under such conditions the amount of cooling gas (argon) used proved to about 6.5 liters/min, while the optimum parameters of the glass sprayer which ensure the best operational conditions of the excitation source changed very little. The gas pressure at the sprayer inlet was 2.5 atm, while the amount of solution used was 6-8 ml/min. The distance between the electrodes was kept constant at 3 mm. Both carbon electrodes were changed after obtaining three successive spectra belonging to a standard or to a test sample. The generator was operated from a 20 amp dc arc at a voltage of 270 v. The standard solution or the test sample converted into an aerosol by the sprayer passed together with the cooling gas into the inner cavity of the generator, and thence into the plasma stream.

The analytical lines of the elements, and the position of the operating part of the plasma stream were chosen in accordance with the results of preliminary experiments (Fig. 1) so that determination of all the elements could be realized for one (unchanged for the various elements) position of the spectrograph slit relative to the chosen operating part of the plasma stream. The distance in this case was 22 mm. The operating part of the plasma stream located at this height was projected through a one lens illumination system onto the slit of an ISP-22 spectrograph.

The analytical lines used in this work and the excitation energies corresponding to them are given in Table 1.

The spectra were photographed on spectrographic plates type II with a sensitivity of 16 GOST units, and were developed in D-19 developer.

The preliminary exposure was 20 sec, while the main exposure was 75 sec. The spectrograms obtained after photographing the standard solutions and the alloy samples were measured photometrically on a MF-2 microphotometer. The extent of the stability of the photometer readings for some of the lines of the different elements is shown by the curves in Fig. 7. Calibration curves were constructed within the coordinates $\Delta S - \log c$. They are shown in Fig. 8. They are linear over a wide concentration range.

The mean arithmetic error for the reproducibility of spectrographic determination, calculated from three parallel measurements, varies within the limits 3-4%.

In order to check on the accuracy of analysis by the technique described, a group of standard alloys which had been reliably analyzed in seven chemical laboratories was used; these samples were kindly presented to us by K. A. Sukhenko to whom we should like to express our thanks. The mean results of the analyses of these samples which we carried out are compared with the results of chemical analyses in Table 2.

As is evident, the degree of agreement between the results obtained by the two methods can be regarded as completely satisfactory.

SUMMARY

A method has been developed for the quantitative spectrographic determination of impurities and alloying additions in titanium alloys using a plasma generator. The alloys are brought into solution in order to carry out the analyses. The mean arithmetic error of the reproducibility in three parallel determinations is 3-4% (relative). The deviation between the results obtained by this method and by chemical analysis is of the same order.

The excitation conditions of the spectra of various elements in this source have been studied systematically, and the effect of the ionization potentials of the elements, the excitation energy of the spectral lines, the source temperature, the presence in solution of organic materials, and the presence of cations and anions of other elements on these excitation conditions has been established.

Differences in the excitation conditions of the spectral lines of the elements in different zones of the plasma generator stream have been established.

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SEPARATION OF ALKALI METAL IONS AND ISOLATION OF MAGNESIUM IONS FROM THEM BY ELUANT CHROMATOGRAPHY

G. L. Starobinets and G. S. Martinchik

Institute of General and Inorganic Chemistry, Academy of Sciences,
Belorussian SSR, Minsk

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Despite the successes achieved in the ion exchange chromatography of the alkali metals [1-3], there is still a number of important questions which demand further study.

In none of the published papers devoted to the study of the effect of such factors as the particle size of the ion exchange resin, the length of the ion exchange column, elution rate, and the ratio of the components of the synthetic mixtures, on the efficiency of separation, has consideration been given to the question of the criteria which should be followed in choosing an ion exchange resin which is suitable for carrying out eluant chromatography of the alkali metals. Apparently, no one has completely separated mixtures of all the alkali metals, while the most successful separation has only been effected by using not readily available ion exchange resins – Amberlite IR-100, Wofatite KS [4, 5] – or special resins Wofatite KPS-200 [6]. Good separation of mixtures of sodium and potassium has been achieved on KU-2 containing a high divinylbenzene content [7] and on colloidal Dowex-50 [8], but lithium was only separated from sodium and potassium on this resin with difficulty [9] by increasing its dispersivity sharply, a factor which complicates operation since it is necessary to create a vacuum in the lower part of the column. An even more difficult problem is separation of potassium–rubidium and rubidium–cesium mixtures, because of the very close values of the radius of the hydrated ions [10]. Apparently, only Kayas [4] has been successful in quantitatively separating potassium from rubidium; in the paper published earlier by Cohn and Cohn [11] this separation was not quantitative.*

Papers have been published on the separation of mixtures of lithium and magnesium [12], and also of mixtures of magnesium, sodium, and potassium [8], but separation of magnesium from a mixture of all the alkali metals has not been studied.

In the present article a description is given of a method which has been developed for the eluant chromatographic separation of mixtures of all five alkali metals, and also of mixtures of the alkali metals with magnesium, using readily available cation exchange resins–sulfonated polybutadiene resins. A study of the selectivity of the proton – alkali metal cation equilibrium exchange on these cation exchange resins and on KU-2 has enabled us to give some indications on the choice of cation exchange resin suitable for successfully separating mixtures of the alkali metals by eluant chromatography.

EXPERIMENTAL

The selectivity of the proton–cation equilibrium exchange. We studied the selectivity of the equilibrium exchange** on two polybutadiene cation exchange resins–sulfonated polybutadiene rubber (ion exchange resin SKB) and on a sulfonated polybutadiene vulcanizate containing 4% combined sulfur per 100 parts by weight of polymer (cation exchange resin SBR × 4) – and also on the cation exchange resin KU-2 containing 4 nominal percent divinylbenzene. The preparation and properties of the sulfonated polybutadiene have been described in [3]. The exchange capacity of SKB and SBR × 4 with respect to sodium chloride is 2.5 and 2.1 mg. equiv per g of dry resin respectively. For the study of equilibrium exchange carried out at room temperature and at an ionic strength of the equilibrium solution of 0.1, the technique described in the literature [14] was adopted. Since we worked with chlorides, the content of alkali metal in the equilibrium solution and in the resin phase was determined by Mohr's chloride method. The experimental results are shown in Figs. 1 and 2 as partition curves of the ions between the resin and equilibrium solution phases within the coordinates, equivalent fraction of the metal ion in the resin phase $(\bar{x}_M)$ – equilibrium fraction of the ion in the equilibrium solution phase (x_M).

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* New possibilities of separating alkali metals which are opened up by the use of cation exchange resins containing weakly acid groups, e.g., the Russian phosphoric acid cation exchange resin RF, are pointed out in the review by M. M. Senyavin [1].

** A. N. Pokrovskaya and V. S. Soldatov carried out these experiments.

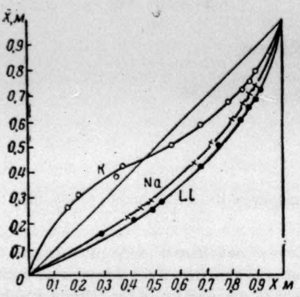

Fig. 1. Distribution of Li, Na, and K between SBR × 4 and solution (in all these diagrams the figure at the side of the symbol for the element denotes the number of mg. equiv. introduced.

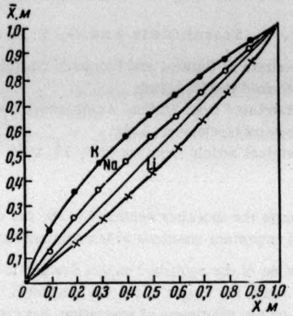

Fig. 2. Distribution of Li, Na, and K between KU-2 and solution.

Free Exchange Energy of the Proton–Cation Exchange in Infinitely Dilute Solutions

Ion exchange resin SBR × 4			Ion exchange resin KU-2	
RM	K_{sol}	−ΔF, cal/g. equiv.	K_{sol}	−ΔF, cal/g. equiv.
RLi	5.0	943	1.5	237
RNa	3.3	699	0.9	−62
RK	2.0	406	0.6	−300

It is clear from the figures that on the resin SBR × 4 (SKB behaves in a similar fashion) the partition curves of the ions between the phases (with the exception of potassium in dilute solutions) lie below the diagonal of the square $\bar{x}_M - x_M$, i.e., the selectivity coefficient of the proton–cation equilibrium exchange which is equal to the ratio of the equivalent fractions of hydrogen ions and metal ions in the resin phase divided by the same ratio in the equilibrium solution phase [15] is greater than unity.* On the cation exchange resin KU-2, as is evident from Fig. 2, the selectivity coefficient during the exchange of lithium for protons is greater than unity throughout the whole range of compositions, while for the exchange of sodium and potassium for protons it is less than unity.

The values of the partition coefficients of hydrogen ions for the cation exchange resins SBR × 4 and KU-2 in the corresponding metal forms are given in the table, they are equal to the tangents of the slopes of the partition coefficients at $x_M = 1$. The same table contains the values of the maximum work of transferring a g. equiv of hydrogen ions from an infinitely dilute solution into the ion exchange resin in the metal form; these values are expressed in calories per g. equiv. and are calculated by means of the equation:

$$A = -\Delta F = RT \ln K_p.$$

It is clear from the results given in the table that the ratio of the partition coefficients in both resins is approximately the same for this series of ions. However, in the case of the resin SBR × 4 (and also in the case of SKB) the transfer of hydrogen ions from an infinitely dilute solution into the metallic form of the resin is a spontaneous process, while in the case of KU-2 this process is only spontaneous for the resin in the lithium form.

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* S-shaped partition curves similar to the curve for potassium in Fig. 1 can be obtained on cation exchange resins containing different types of functional groups [16]. The polyfunctionality of sulfonated polybutadienes has been established in [13].

This is an important factor for realizing eluant chromatography. In fact, since the elution process proceeds spontaneously on sulfonate polybutadiene resins even in infinitely dilute solutions of acids, the choice of an eluant when using resins of this type is a relatively simple operation; it is necessary to start elution with very dilute acid solutions and then by gradually increasing the acid concentration it is possible to obtain constricted but not overlapping zones for the individual ions.

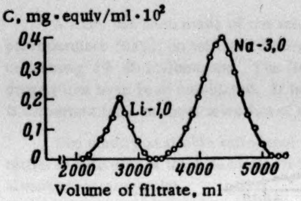

Fig. 3. Separation of Li and Na on KU-2.

For separation of alkali metal cations (with the exception of lithium) on the cation exchange resin KU-2 there is no point in starting a search for eluants with very dilute solutions of acids, while it is necessary to find empirically, or by calculation by means of the isotherms of the chemical reactions, that acid concentration (naturally this will have a particular value for each of the ions in a mixture) at which the hydrogen—cation exchange will become a spontaneous process.[*] This fact transforms the empirical choice of eluants for ion exchange resins of the KU-2 type into a vague problem, and even under the best conditions into a very difficult operation.

In agreement with the considerations outlined above, it has been found possible to separate sodium and potassium ions on Dowex-50 by means of fairly concentrated acid −0.7 N HCl [8], while attempts to separate a ternary mixture of lithium—sodium—potassium with the same eluant proved to be very difficult, as noted already. From a thermodynamic point of view such an attempt is unfounded, since at such a hydrogen ion concentration, the exchange process is spontaneous for all three cations. As is obvious from the results given in the table for KU-2, separation of mixtures of lithium and sodium should be carried out with acid whose concentration is such that the hydrogen—sodium exchange has not yet become a sharply spontaneous process. These ideas have been confirmed experimentally. We were able to separate, without any difficulty, mixtures of lithium and sodium on KU-2 containing 4% divinylbenzene and consisting of coarsely dispersed spherical particles with a particle size of 0.25-0.50 mm in a column of 1 × 100 cm, using 0.05 N HCl at the rate of 3 ml per minute. The results of one of these experiments,[**] in which a mixture containing 1 mg. equiv. of lithium and 3 mg. equiv. of lithium was separated, are shown in Fig. 3.

A characteristic feature is that the most successful experiments in separating mixtures of the alkali metals have been carried out by means of dilute acids. Thus Kayas [4] used 0.1 N HCl on Amberlite IR-100, Wickbold [5] used 0.1 N HCl on Wofatite KS, while Jentzsch and Frotscher [6] used 0.01 N HCl on Wofatites KPS-200 and F. There is a basis for assuming that the resins mentioned are characterized, like the sulfonated polybutadiene resins, by the fact that the hydrogen—cation exchange proceeds spontaneously on them from infinitely dilute solutions of acids.

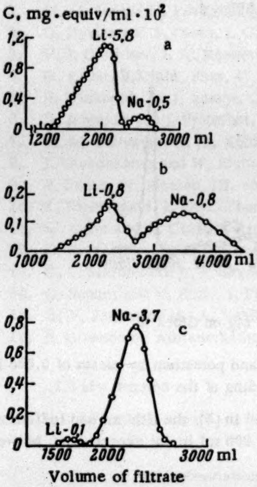

Fig. 4. Separation of mixtures of Li and Na on SBR × 4. a) Li : Na = 11.6 : : 1; b) Li : Na = 1 : 1; c) Li : Na = 1 : 37.

Thus in order to separate mixtures of ions successfully by eluant chromatography, on the basis of an empirical choice of the hydrogen ion concentration of the eluants, it is extremely important that in addition to marked differences in the values of the selectivity coefficients of the hydrogen—cation exchange equilibrium, this exchange should be spontaneous in the region of infinitely dilute solutions of hydrogen ions.

Experiments on chromatographic separation. In order to obtain results comparable to those given in the literature, the experiments on chromatographic separation were carried out under conditions analogous to those used by Wickbold [5] and Jentzsch and Frotscher [6]. The column whose dimensions were 1 × 100 cm, contained 56-59 g of ion exchange resin with particle size 0.1-0.25 mm. The elution rate was 5 ml per minute. In Fig. 4 are shown elution curves obtained during the separation of mixtures of lithium and sodium in various proportions, 0.025 N HCl being used as the eluant.

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[*] It is necessary, however, in order to carry out these calculations, to have data on the activity coefficients of the components.

[**] Carried out by N. A. Polyak.

It is clear from the diagram (curve "c") that the separation is still quite clear cut when the lithium content is less than 3% of the mixture. Separation of mixtures of sodium and potassium is even better. In Wickbold's paper [5] sodium and potassium gave a mixed zone when their contents in the mixtures were in the proportion 1 : 9.

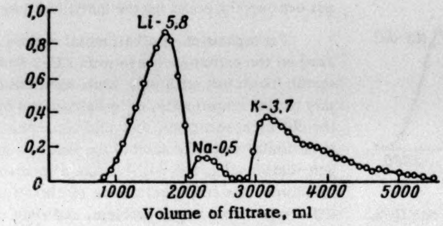

Fig. 5. Separation of mixtures of Li, Na, and K on SBR × 4.

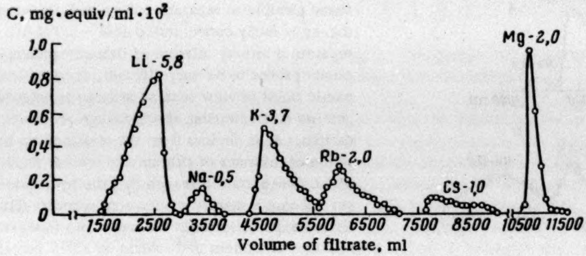

Fig. 6. Separation of mixtures of Li, Na, K, Rb, Cs, and Mg on CBR × 4.

Figure 5 shows the results obtained during separation of lithium, sodium, and potassium by means of 0.025 N HCl passed through the column at a rate of 5 ml/minute, when the relative loading of the column was 0.1.

The clearness of the separation is approximately the same as that obtained in [5]; the lithium and sodium zones almost touch each other, while there is a considerable gap, amounting to about 200 ml in our experiments, between the sodium and potassium zones.

During separation of a mixture of all five alkali metals, sodium and lithium were eluted with 0.025 N HCl, while rubidium was eluted with 0.05 N HCl, and cesium with 1.0 N HCl. During separation of the given component mixture the elution rate had to be dropped to 2 ml/min, since at higher elution rates potassium and rubidium gave a small mixed zone.

We established during the course of a large number of experiments that separation is most clear cut on the cation exchange resin SKB: there is an appreciable gap between the lithium and sodium zones, while the sharpness with which potassium and rubidium are separated also increases. Comparison of the results of experiments carried out on SKB with the results given in [5] and [6] shows that the partitioning capacity of SKB is slightly greater than that of Wofatite KS, and considerably higher than that of Wofatite F, and is only inferior to Wofatite KPS-200. A slight drawback of sulfonated polybutdiene resins is the necessity of using comparatively large volumes of eluent during elution of the alkali metals from the column. However, when working with small amounts of components in the mixtures (of the order of some tenths of a mg. equiv.), and particularly when using automatic collectors, this drawback is unimportant.

Compared with other divalent cations, it is known that [9] magnesium is the most difficult element to separate from the alkali metals by ion exchange chromatography. Mixtures of all the alkali metals and magnesium were separated very well on the sulfonated polybutadiene resins studied in the present work.

Elution curves for a mixture of all the alkali metals and magnesium are shown in Fig. 6. Lithium and sodium were eluted with 0.025 N HCl, potassium with 0.05 N HCl, rubidium with 0.085 N HCl, cesium with 0.1 N HCl, and magnesium with 0.5 N HCl.

SUMMARY

A study has been made of the selectivity of the proton—alkali metal cation exchange equilibrium on sulfonated polybutadiene (SKB), on sulfonated polybutadiene vulcanizate containing 4% combined sulfur (SBR × 4), and on KU-2 containing 4% divinylbenzene. The free energies of the proton—cation exchange in infinitely dilute solutions of hydrogen ions have been calculated. It has been shown that the sign of the free energy of the proton—cation exchange is important for a rational selection of eluants.

The readily available sulfonated polybutadienes — SKB and SBR × 4 are quite suitable for the quantitative separation of mixtures of the ions of all five alkali metals, and also for the separation of these ions from magnesium by eluent chromatography.

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DETERMINATION OF SMALL AMOUNTS OF POTASSIUM BY AN ISOTOPE DILUTION METHOD

Yu. A. Shukolyukov and I. I. Matveeva

Laboratory of Precambrian Geology, Academy of Sciences, USSR, Leningrad

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There are no satisfactory methods at present for the determination of about 0.001 g of potassium in one g of rocks and minerals with an accuracy of down to 2-3%. In order to determine the absolute age of a specimen, development of techniques for the determination of small amounts of potassium is of great practical importance. A solution of this problem would allow one to determine age by the argon method on the basis of primary rocks with a potassium content of less than 1%. The use of the isotope dilution technique would appear to be the most promising approach. Using such a technique it should be possible to achieve a considerably higher sensitivity and accuracy than is possible by ordinary chemical methods. We set ourselves the problem of developing a method for the determination of potassium by means of the MI-1305 mass-spectrometer, and comparing the results obtained with the results of chemical determinations. We chose samples with a low potassium content for study: diabases, beryls, and tourmalines. The diabases were decomposed by the usual method [1]. The difficulties involved in decomposing beryls and tourmalines led us to use a special chemical method for their treatment.

Technique for the chemical analysis of beryls and tourmalines. On clinkering tourmalines and beryls by the classical Lawrence–Smith method an appreciable part of the sample remains undecomposed. We tried to determine potassium quantitatively in beryls and tourmalines after using Yashchenko and Barshavskii's rapid method [1]. For determining potassium by this method micas are decomposed with a mixture of hydrofluoric and oxalic acids. Beryls and tourmalines, however, are not completely decomposed by this method. On the basis of the work of Tananaev and Smyshlyaev [2], the authors, on Yashchenko's advice, have modified this method. Decomposition with the mixture of hydrofluoric and oxalic acids was replaced by sintering of the minerals with ammonium fluoride, and subsequent decomposition of the fluorides with oxalic acid. Ammonium fluoride is a more active reagent. During decomposition of the minerals, in order to make the analysis quantitative, the samples must be given repeated treatment with ammonium fluoride. Decomposition of the fluorides and silicofluorides formed with oxalic acid, and the subsequent analytical procedure were carried out in the same way as in the method published earlier [1]. The complete analytical procedure which we followed is given below.

The test samples were ground as carefully as possible, since completeness of decomposition depends on the degree of grinding. A 1 g aliquot was placed in a platinum basin and mixed with ten times its amount of ammonium fluoride. The basin was placed on a flask heater, and sintered at 300-400°. Ammonium fluoride reacts vigorously over this temperature range with silicate powder, and the sample is decomposed in a matter of a few minutes. A further 2-3 g of NH_4F was added to the fluorides formed and sintering repeated. Six-seven g of oxalic acid was added to the dry residue; this was followed by addition of hot water, and the contents of the basin evaporated on a water bath to dryness. The dry residue was again moistened with hot water and the evaporation repeated. The platinum basin was then transferred onto a sand bath, where the oxalic acid fused and started to decompose. Oxalic acid was finally removed and decomposed on a flask heater at 250°.

Hot water was added to the dry residue, and 5-6 ml of concentrated HNO_3 and 8-10 ml of $HClO_4$ added. The basin was placed on a water bath and evaporated until perchloric acid fumes started to come off; it was then placed on a sand bath on which the residue was evaporated to a moist state. On cooling the basin, the mass was extracted. A slight excess of perchloric acid is necessary for preventing formation of basic salts.

The residue was dissolved in hot water, transferred to a beaker, and boiled for 2-3 min. Traces of silica, and other insoluble acids which may be present (titanic, niobic, tantalic acids etc.) were filtered off. A further 5-6 ml of $HClO_4$ was added to the solution in order to ensure complete removal of nitric acid and to obtain pure perchlorates.

The solution was again evaporated in succession on a water bath and on a sand bath to the moist salt stage, the salts were treated with a few 25-30 ml portions of ethanol (rectified) containing $HClO_4$ (400 ml of C_2H_5OH + 2 ml of 40% $HClO_4$). The ethanol solution of the perchlorates was poured off through a filter. The total volume of ethanol was about 100 ml. The residue consisting in the main of $KClO_4$, in the beaker and on the filter, was dissolved in hot water, 0.05-1.0 ml of $HClO_4$ was added to the solution, and the solution again evaporated to the moist salt state, the salts were again treated 6-8 times with absolute ethanol containing $HClO_4$, smaller portions of the ethanol solution being used this time. The $KClO_4$ precipitate was dissolved in water and transferred to a small tared platinum basin. The solution was evaporated to dryness on a water bath. Potassium perchlorate was finally dried for 30 min in an oven at 350° and weighed. The conversion factor to potassium is 0.2822. A complete analysis takes 10-12 hr.

Isotope dilution method. Potassium enriched with K^{41} to the extent of about 100 times was used as the stable indicator. The amount of potassium m_0 in the test sample is found by means of the formula:

$$m_0 = m_n \cdot \frac{M_0}{M_n} \cdot \frac{n_c - n_n}{n_0 - n_c} \cdot \frac{1 + n_0}{1 + n_n}, \tag{1}$$

where m_n is the amount of indicator with a ratio of the isotopes $K^{39}/K^{41} = n_n$, n_0 is the ratio of K^{39}/K^{41} in the sample n_c is the same ratio for the mixture, M_0 and M_n is the atomic weight of potassium in the sample and in the indicator.

In order to determine potassium with a relative error of about 3% the values of the ratios of the isotopes should be known to an accuracy of down to 1%. Published results on the isotopic composition of reagent and natural potassium are contradictory.

According to results given by various authors, the value of K^{39}/K^{41} changed in the samples tested from 12.6 to 14.6 [3-14].

However, as shown in [13] and [14], the scatter of the results is not caused by the natural fractionation of the isotopes. Various research workers have used different ion sources for ionizing the potassium: 1) a ribbon ionizer with a very thin layers of potassium salts or oxide amounting to $\leq 10^{-6}$ g; 2) a ribbon with a dense solid or fused salt, or with oxide, amounting to $n \cdot 10^{-4}$ g; 3) a pure or oxidized metal surface saturated with potassium; 4) metallic potassium or its oxide as vapor.

In the case of a source of type 1, the value of K^{39}/K^{41} changes according to a law similar to the law of molecular diffusion of a gas through an aperture into a vacuum. Discrimination according to the masses corresponding to the value $\sqrt{39/41}$ occurs. The measured ratio K^{39}/K^{41} decreases with time during an experiment.

When using ionic sources types 2 and 3 the main role is played by diffusion inside the melt or crystalline lattice. When $> 10^{-3}$ g potassium is placed on the ribbon, the ratio K^{39}/K^{41} changes regularly with time up to the point at which an equilibrium state is reached [10, 13, 14]. On placing $10^{-5} - 10^{-4}$ g of pure potassium salt on the ribbon it was found that the change in the ratio K^{39}/K^{41} during an experiment is less than 1%. We took this into account when placing the sample on the ribbon.

Measurements were made on the standard MI-1305 mass-spectrometer. A single beam method of measurement was adopted. Surface ionization on tungsten was used. Tungsten ribbons, as was established, contain a relatively large amount of potassium which gives rise to a "background" to the 39 and 41 masses. In order to purify the ribbons they were calcined beforehand for 2-3 hr outside the mass-spectrometer at 1450° in a vacuum of about 10^{-5} mm Hg.

Before each experiment the ion source was carefully washed in 2% HCl solution, distilled water, and ethanol. As a rule, after calcining the ribbons and washing them, the background did not exceed 0.1% of the values of the K^{39} and K^{41} peaks. A few drops of the test solution of K_2SO_4 was then placed on a tungsten ribbon. The ribbon was dried under an infrared lamp, after which the ion source was placed in the mass-spectrometer. About $5 \cdot 10^{-5}$ g of potassium is required for an analysis. Thirty-fifty measurements of the ratios of the K^{39} and K^{41} isotopes were made in each experiment.

Determinations of the ratio K^{39}/K^{41} in potassium from reagents were also made, an oven ion source and ionization with electrons being used. A value of 13.95 was obtained. This does not differ appreciably from the result found on using the surface ionization method (Table 1).

It is clear from Table 1, that the isotopic composition of potassium was identical in all the natural samples we measured, and coincided with the isotopic composition of reagent potassium: $K^{39}/K^{41} = 13.92 + 0.09$. This value does not differ from that of Reutersward which he obtained under similar measurement conditions —13.88 + 0.07 [13].

An indicator solution ($K^{41}Cl$) of known concentration was prepared for quantitative determination. For this purpose a subsidiary solution of reagent K_2SO_4 was prepared. It was standardized gravimetrically; aliquots of the solution were accurately weighed out, evaporated to dryness, and the weight of dry salt determined.

Weighed volumes of the subsidiary solution and the indicator potassium solution were then mixed. From the measured katio K^{39}/K^{41} in the mixed solution it was possible to calculate the titer of the solution of the indicator potassium solution.

TABLE 1

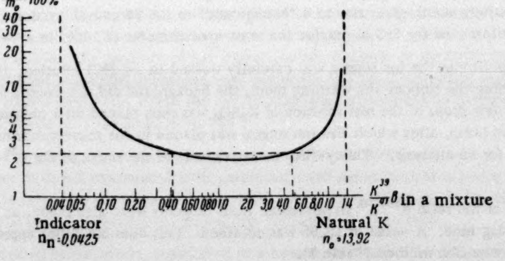
Sample	K^{39}/K^{41}	Sample	K^{39}/K^{41}
Reagent K_2SO_4	13.92 ± 0.09	Beryl B	13.84 ± 0.10
Reagent KCl		Tourmaline A	13.80 ± 0.08
(Oven source)	13.95 ± 0.07	Beryl K-300	13.80 ± 0.10
Beryl 993	14.10 ± 0.10	Muscovite K-300	13.77 ± 0.08

The procedure adopted for the isotope dilution technique was as follows: decomposition of an aliquot with ammonium fluoride was carried out as indicated above. An accurately weighed amount of the indicator solution was added to the basin containing the sinter.

For establishing the amount of indicator solution that should be added, the following fact should be borne in mind. The error in determining the amount of potassium in a sample is given by the expression (obtained as usual from formula 1):

$$\frac{\Delta m_o}{m_o} \approx \frac{\Delta T_n}{T_n} + \frac{\Delta B_n}{B_n} + \frac{(n_o - n_n)\cdot \Delta n_c}{(n_c - n_n)\cdot(n_o - n_c)} + \frac{(1 + n_c)\,\Delta n_n}{(n_c - n_n)\cdot(1 + n_n)} + \frac{(2n_o - n_c + 1)\cdot \Delta n_o}{(n_o - n_c)\cdot(1 + n_o)}\,, \qquad (2)$$

where T_n is the titer of the indicator, B_n is the weight of indicator solution taken. The value of $\Delta B_n/B_n$ is much less than the sum of the remaining terms on the right hand side of expression 2. Variations in the error in weighing the indicator solution, for different value of B_n, do not affect the total error Δm. Accordingly, for a given indicator with a titer T_n and under conditions such that n_0 = const an n_n = const the error in determining potassium is only a function of one term n_c. The function $\Delta m/m_0 = F(n_c)$ which we calculated is shown graphically in the diagram. Analysis of this curve shows that the minimum error in determining potassium is observed under conditions for which the ratio of the isotopes K^{39} and K^{41} in a mixture is near 1 (n_c about 1). For the range $0.4 \leq n_c \leq 5$, the error does not exceed ± 2.5%. Starting with a natural sample, one can get a rough (with an accuracy of an order) idea of its expected potassium content, and thereby take a suitable amount of indicator solution so that the condition $0.4 \leq n_c \leq 5$ is obeyed. After adding the indicator to the basin, oxalic acid was added. The subsequent procedure was the same as that described above, the only difference being that the yield of potassium may be less than 100%.



The relationship between the error in determining potassium and the ratio K^{39}/K^{41}.

The perchlorates obtained during the final analytical stage were converted to the sulfates in the platinum basin. The sulfuric acid was carefully removed by heating. A few drops of water when then added to the contents of the basin. The solution was placed on the ribbon of the ion source by means of a capillary.

The reproducibility of the experimental results obtained by the isotope dilution method are illustrated in Table 2.

TABLE 2.

Sample (weight 1 g)	Amt. of indicator solution added, g	K^{39}/K^{41}	K, %	K_{mean}, %	Error, %
Diabase № 2062	0,9228	3,31	0,294	0,294±0,001	±0,3
» № 2062	0,8526	3,59	0,295		
» № 2177	0,7148	3,34	0,226	0,224±0,002	±0,9
» № 2177	0,7002	3,37	0,222		
» № 2101	0,6508	3,83	0,257	0,255±0,002	±0,8
» № 2101	0,9460	2,90	0,253		
» № 2247	0,6480	2,17	0,116	0,114±0,002	±1,8
» № 2247	0,8744	1,64	0,112		
» № 2247	0,7082	1,86	0,115		
» № 2159	0,8404	3,85	0,319		
» № 2159	0,5954	2,92	0,339	0,329 ±0,007	±2,1
» № 2159	1,221	2,80	0,329		
Tourmaline A	1,2481	2,31	0,237	0,242±0,005	±2,1
» »	1,5990	1,94	0,247		
Beryl K-300	1,1014	1,56	0,117	0,116±0,001	±0,9
	1,0216	1,63	0,114		

TABLE 3

Sample	K found, %		
	by the perchlorate method		mass-spectrometric method
	decomposition with $HF + H_2C_2O_4$	decomposition with with $NH_4F + H_2C_2O_4$	
Diabase № 2177	0,26±0,02		0,224±0,002
» № 2101	0,23±0,02		0,255±0,002
» № 2247	0,11±0,02		0,114±0,002
» № 2159	0,31±0,02		0,329±0,007
Tourmaline A		0,20±0,02	0,242±0,005
» 1551		0,21±0,02	0,218±0,004
Beryl K-300		0,09±0,02	0,116±0,001
» № 993		0,15±0,02	0,145±0,003
» B		0,22±0,02	0,206±0,006

The potassium contents given in Table 2 have been corrected for the amount of potassium in the reagents. In the case of diabases the correction was about 1% of the potassium content, while for beryls and tourmalines it amounted up to 15%.

Results of the determination of potassium in minerals by two methods – chemical and mass-spectrometric – are compared in Table 3.

The slight scatter in the results obtained by the two methods can be explained by the insufficient accuracy of the chemical method at low potassium contents in the minerals. It is obvious that the results obtained by the isotope dilution method are more reliable.

Potassium was also determined by isotope dilution in mica with a known potassium content. Chemical and mass-spectrometric determinations gave results in satisfactory agreement with each other.

In muscovite K = 300, the amount of potassium determined chemically was 8.28 and 8.30%, while by the mass-spectrometric method the value found was 8.13 and 8.36%.

In conclusion we should like to thank E. K. Gerling and M. L. Yashchenko for their continued interest and their help in the work.

SUMMARY

A method used for the quantitative chemical decomposition of tourmalines and beryls which are difficult to breakdown has been improved; the improved method ensures complete separation of potassium for analysis.

It has been shown that a mass-spectrometric method is suitable for the quantitative determination of potassium in minerals at a potassium concentration in the latter of less than 1%.

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GRAVIMETRIC DETERMINATION OF SCANDIUM WITH PHENYLPHOSPHINIC ACID

I. P. Alimarin, V. I. Fadeeva, and T. N. Petrova
M. V. Lomonosov Moscow State University

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Scandium has a clearly expressed affinity toward phosphate ions. It forms sparingly soluble compounds with different phosphoric acid derivatives. Vickery's work [1] which involved the use of the radioactive isotope Sc^{46}, has shown that of all phosphoric acid derivatives, only disodium and phosphates and phytin precipitate scandium quantitatively. Vickery has also shown that scandium is not precipitated quantitatively as its hydroxide, oxalate, carbonate, or fluoride. Sodium pyrophosphate suggested by Beck [2], and subsequently studied in detail by Petru [3], does not give satisfactory results, since the precipitate partially dissolves in excess of reagent, and hydrolyzes during washing. Organic derivatives of pyrophosphoric acid, such as phytin, salts of the ester of aneurinepyrophosphoric acid and adenyltriphosphoric acid [4] form very sparingly soluble neutral salts with scandium. When precipitation is carried out with the reagents indicated, gravimetric forms are not obtained; these reagents are only used for separating and detecting scandium.

Recently, Bomberger [5] suggested hypophosphoric acid for the quantitative isolation and gravimetric determination of scandium. Materials which oxidize hypophosphoric acid, particularly nitrate ions, interfere.

Phenylphosphinic acid, the reagent which we should like to suggest, permits scandium to be precipitated quantitatively, while the precipitates obtained can be weighed after they have been dried at 120°.

TABLE 1. Composition of the Precipitate of Scandium Phenylphosphinate

$Sc_2(C_6H_5PO_2)_3 \cdot 3H_2O$	Content, %			$Sc_2(C_6H_5PO_2)_3 \cdot 3H_2O$	Content, %		
	calc.	by chemical analysis	by thermogravimetric analysis		calc.	by chemical analysis	by thermogravimetric analysis
C	35,29	34,5	35,6	H	3,44	3,7	
P	15,18	15,1		O	31,36		
Sc	14,73	14,5		H_2O	8,82		8,9

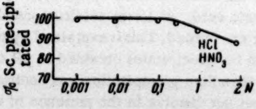

Fig. 1. Completeness of precipitation of scandium as a function of acid concentration.

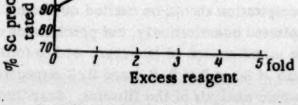

Fig. 2. Effect of excess reagent on precipitation of scandium.

Phenylphosphinic acid $C_6H_5PO(OH)_2$ reacts with scandium in an acid medium to form a white amorphous precipitate, which is soluble in dilute sulfuric acid, concentrated nitric and hydrochloric acids, and also in a saturated oxalic acid solution. Phenylphosphinic acid gives a visible turbidity at a scandium concentration as low as 15 μg Sc/ml.

The solubility of scandium phenylphosphinate is less than that of scandium phytate, and is equal to 10^{-7} M. A photometric method with xylenol orange was used for determining the solubility of the precipitate in water.

The composition of the air-dry precipitate os candium phenylphosphinate was established by thermogravimetric and chemical analysis (Table 1). The thermogram shows that the water is combined in a stoichiometric proportion in the precipitate of scandium phenylphosphinate, while it also shows that the weight of the precipitate remains constant over the range 140-240°, the precipitate starts to decompose at 250°; $Sc(HPO_4)_3$ is formed at 900°.

The fact that the composition of the precipitate remains constant, and the fact that the precipitate readily looses its water of crystallization at 120-160° mean that $Sc_2(C_6H_5PO_3)_3$ can be weighed directly (conversion factor 0.1616).

TABLE 2. Precipitation of Scandium with Phenylphosphinic Acid

Sc, mg		Error, mg	Media
taken	found		
5,91	5,90	—0,01	0.1 N HCl or HNO_3
7,24	7,20	—0,04	
11,82	11,78	—0,04	
5,91	5,88	—0,03	0.1 N HCl and a 2% solution of tartaric acid
7,24	7,22	—0,02	
11,82	11,79	—0,03	
2,95	2,89	—0,06	0.1 N HCl and a 2% solution of citric acid
5,91	5,90	—0,01	
7,24	7,20	—0,04	

TABLE 3. Determination of Scandium in the Presence of the Rare Earths

Ratio Sc: rare earths	Sc, mg		Error, mg	Ratio Sc: rare earths	Sc, mg		Error, mg
	taken	found			taken	found	
1 : 10	5,91	5,94	+0,03	1 : 100	2,95	3,04	+0,09
	7,24	7,30	+0,06		5,94	5,94	0,00
	11,82	11,82	0,00		7,24	7,23	—0,01

In order to establish the optimum conditions for precipitating scandium with phenylphosphinic acid we investigated the effect of the concentration of various mineral acids. For this purpose various amounts of hydrochloric or nitric acid were added to a standard hydrochloric acid solution of a scandium salt, the solution was diluted to 50 ml and heated almost to the boil, and scandium was then precipitated with a 1% solution of phenylphosphinic acid. Solution plus precipitate were kept on a water bath for 15-20 min, and the precipitate filtered off through a No. 4 filter crucible, and washed with a hot 1% ammonium nitrate solution and then with ethanol. The precipitate was dried at 120-140° and weighed as $Sc_2(C_6H_5PO_3)_3$. On the basis of the results obtained (Fig. 1), it was established that precipitation should be carried out from 0.1 N hydrochloric or nitric acid. At lower acidities scandium is still precipitated quantitatively, but precipitates of variable composition are formed. This is explained by the tendency of the scandium ion to hydrolyze and to form polymeric ions [6]. In the precipitates obtained at pH 4 and pH 1, the ratio of Sc to P is 2 : 2.4 and 2 : 3 respectively. Completeness of scandium precipitation was controlled by spectrographic analysis of the filtrates. Scandium phenylphosphinate does not dissolve in the presence of excess reagent; it is sufficient to take a twofold excess of reagent for quantitative precipitation of scandium (Fig. 2). Tartrates and citrates do not interfere with precipitation (Table 2).

On precipitating scandium in the presence of large amounts of the rare earths high results were obtained as a result of the coprecipitation of the latter, despite the fact that the rare earths are not precipitated by phenylphosphinic acid from 0.1 N hydrochloric acid solutions. Tartaric and citric acids prevent coprecipitation of the rare earths.

Scandium was precipitated as follows in the presence of the rare earths. Tartaric (or citric) acid was added to the test solution in such amount that its concentration in the final solution was 2%, hydrochloric acid was then added until the pH was 1, the solution was diluted to 50 ml and was heated almost to the boil when the scandium was precipitated with a 1% solution of phenylphosphinic acid. The results obtained are given in Table 3.

The alkali and alkaline earth elements, zinc, nickel, cobalt, cadmium, and copper do not interfere with scandium determination. Elements such as zirconium, thorium [7], niobium, tantalum, hafnium, and titanium are precipitated together with scandium from strongly acid solutions.

In the presence of oxalate ions, when the stable anions $[Sc(C_2O_4)_3]^{3-}$ are formed, phenylphosphinic acid does not precipitate scandium, it does, however, precipitate zirconium, but not quantitatively.

SUMMARY

Phenylphosphinic acid, which forms a precipitate having the composition $Sc_2(C_6H_5PO_3)_3 \cdot 3H_2O$ with scandium, is suggested for the determination of the latter. The form in which it is weighed $Sc_2(C_6H_5PO_3)_3$ is obtained after drying the precipitate at 120-160°. In the presence of tartaric or citric acid, phenylphosphinic acid can be used for separating scandium from the rare earths.

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POTENTIOMETRIC DETERMINATION OF TRIVALENT THALLIUM WITH DIVALENT VANADIUM

S. I. Gusev and L. A. Ketova

Perm State Medical Institute

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Solutions of divalent vanadium salts can be used for the potentiometric determination of a series of cations [1]. On the basis of the values of the normal potentials $V^{3+}/V^{2+} = -0.20$ v and $Tl^{3+}/Tl^{+} = +1.22$ v, one can assume that trivalent thallium should be reduced by solution of divalent vanadium salts. The present article is devoted to the results obtained during a study of the stoichiometric ratios during the interaction of trivalent thallium and divalent vanadium, while the possibility is demonstrated of using the latter for the quantitative determination of thallium.

EXPERIMENTAL

A VCl_2 (or VSO_4) solution was prepared by reducing ammonium vanadate with amalgamated zinc. An acid solution of a divalent vanadium salt keeps its titer for more than 20 days in the apparatus described by Busev and Li Gyn [2]. The VCl_2 solution was standardized potentiometrically against bismuth oxide. A solution of a trivalent thallium salt was prepared by dissolving a known amount of thallous acetate in water and acidifying the solution with sulfuric acid. The univalent thallium was oxidized with free chlorine, excess of which was removed by boiling. The solution obtained was diluted with water in a standard flask, and its concentration determined by means of diantipyrylmethane [3].

Potentiometric titration was carried out on a P-4 potentiometer, the reference electrode was a saturated calomel electrode, while the indicator electrode was a platinum wire. During thallium determination the vanadium solution was added from a microburet with scale divisions of 0.02 ml.

As experiment showed, trivalent thallium oxidizes divalent vanadium to the trivalent state. During potentiometric titration of a known volume of a trivalent thallium salt solution with a solution of divalent vanadium chloride or sulfate in a CO_2 atmosphere, at room temperature, a sharp potential jump (up to 600 mv) is observed at the end point. Satisfactory results were obtained on titrating solutions of trivalent thallium salt with 0.05 N VCl_2 in a medium of 6-10 N hydrochloric or sulfuric acid (Table 1).

On the basis of the results obtained the following potentiometric method has been developed for the determination of trivalent thallium.

Concentrated HCl or H_2SO_4 is added to a solution containing a trivalent thallium salt until the acid concentration is 6-10 N; CO_2 is bubbled through the solution which is titrated with 0.05 N VCl_2 solution until the platinum electrode gives a potential jump. Large amounts of Cd, Zn, and Pb (Table 2) do not interfere with determination of thallium. Precipitation of $PbCl_2$ does not interfere with titration. Fe^{3+} and Cu^{2+} ions, and oxidizing agents MnO_4^-, $Cr_2O_7^{2-}$, $S_2O_8^{2-}$ etc.) interfere.

Determination of thallium in bricketted cadmium. An aliquot of cadmium (1.0-1.5 g) is dissolved in 10 ml of 2 N H_2SO_4 and 1 ml of concentrated HNO_3. The solution is heated on a sand bath until the nitrogen oxides have been removed, and the univalent thallium is oxidized with chlorine or ammonium persulfate. Excess oxidizing agent is removed by heating, HCl, or H_2SO_4 is added until the requisite acid concentration is obtained, and the solution titrated potentiometrically with 0.05 N VCl_2 solution.

Determination of thallium in slag. An aliquot of slag is dissolved in 10-15 ml of 0.5 N HNO_3, the thallium is oxidized to its trivalent state in which it is titrated with VCl_2 solution.

In order to check on the accuracy of the results obtained, after the end point had been reached a known amount of a standard solution of trivalent thallium was added and titration continued. Results of such determinations are given in Table 3.

TABLE 1. Potentiometric Determination of Trivalent Thallium with VCl_2 Solution

Thallium, mg		Error, mg	Thallium, mg		Error, mg
taken	found		taken	found	
5,14	5,13	−0,01	2,57	2,60	+0,03
5,14	5,19	+0,05	2,57	2,57	0
4,12	4,10	−0,02	1,03	1,06	+0,03
4,12	4,11	−0,01	1,03	1,03	0

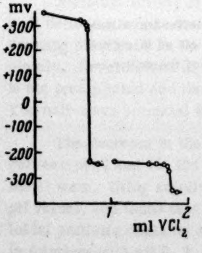
TABLE 2. Determination of Thallium in the Presence of Foreign Cations

Taken, mg				Ratio Tl : Me	Tl found, mg	Error, mg
Tl	Cd	Zn	Pb			
5,14	500	—	—	1 : 100	5,09	−0,05
2,57	250	—	—	1 : 100	2,54	−0,03
3,86	1150	—	—	1 : 300	3,82	−0,04
2,57	1500	—	—	1 : 600	2,60	+0,03
2,57	3000	—	—	1 : 1200	2,64	+0,07
3,86	—	2300	—	1 : 600	3,86	0
5,14	—	—	2600	1 : 500	5,13	−0,01
2,06	600	600	600	1 : 300 : 300 : 300 (1 : 900)	2,11	+0,05
2,06	400	400	400	1 : 200 : 200 : 200 (1 : 600)	2,05	−0,01

TABLE 3. Determination of Thallium in Technical Materials

Sample	Wt. of sample, g	Tl found, %	Tl added, %	Amt. of Tl that should be present %	Tl found, %	Error, %
Bricketted cadmium (containing 0.15% Tl accord- to plant analysis)	1,3062	0,13	0,32	0,45	0,43	−0,02
	1,4028	0,17	0,15	0,32	0,32	0
	1,2216	0,17	0,42	0,59	0,58	−0,01
Slag	0,2142	1,16	0,96	2,12	2,15	+0,03
	0,2344	1,28	1,62	2,90	2,89	−0,01
	0,2308	1,21	1,50	2,71	2,68	−0,03

Determination of thallium in the presence of bismuth. We have already pointed out [1] that bismuth can be quantitatively determined by means of divalent vanadium. Despite the fact that bismuth is quantitatively separated by divalent vanadium from concentrated hydrochloric acid, nevertheless a sharp potential jump is observed during potentiometric titration in a medium of 1-3 N acid.



Titration of a mixture of 3.01 g of thallium and 3.14 mg of bismuth. 2.98 mg thallium and 3.14 mg bismuth found.

Bearing in mind the oxidation potentials of thallium and bismuth, one might expect that at an appropriate acidity, thallium should be reduced first and then bismuth. The technique for determining thallium and bismuth successively reduces to the following. To a solution of a trivalent thallium salt was added a known volume of a bismuth salt solution (or Bi_2O_3), and the acidity of the solution adjusted to the requisite value (6-10 N) for determination of thallium by means of sulfuric or hydrochloric acid. Titration was carried out with 0.05 N VCl_2 until the first potential jump was obtained. The solution was then diluted approximately three times with water and titration continued to the second potential jump corresponding to completion of reduction of bismuth. Since, during the titration of small amounts of thallium with 0.05 N VCl_2 solution, a microburet must be used in order to attain the highest accuracy, while the bismuth content may be many times greater than that of thallium, after the first potential jump (determination of thallium) it is best to continue titration with 0.1 N VCl_2 solution measured out from a macroburet (determination of bismuth). The presence of large amounts of Cd, Zn, and Pb do not interfere with determination of thallium in bismuth. Results of these determinations are given in Table 4. The titration curves are shown in the diagram.

TABLE 4. Determination of Thallium and Bismuth in Each Others Presence

No.	Taken, mg		Found, mg		Error, mg	
	Tl	Bi	Tl	Bi	Tl	Bi
1	3,01	3,14	2,98	3,14	−0,03	0
2	2,57	3,49	2,62	3,54	+0,05	+0,05
3	1,51	301,5	1,53	299,7	+0,02	−1,8
4*	1,51	150,8	1,57	151,1	+0,06	−0,3

*160 mg Pb, 160 mg Cd, and 160 mg Zn were added to the amounts of Tl and Bi indicated.

We should like to thank V. G. Tiptsova a co-worker in Moscow University for her gift of bricketted cadmium and slag.

SUMMARY

It has been established that trivalent thallium can be determined potentiometrically by titration with a solution of a divalent vanadium salt in 6-10 N hydrochloric (sulfuric) acid.

A method has been developed for the successive determination of thallium and bismuth in each others presence.

Large amounts of Zn, Cd, and Pb do not interfere with thallium determination. The method can be used for analysis of industrial materials.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

THE POLAROGRAPHIC BEHAVIOR OF INDIUM IN THE PRESENCE OF TRIHYDROXYGLUTARIC ACID

E. N. Vinogradova and An Ching-Ju

M. V. Lomonosov Moscow State University

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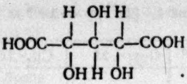
Compound of metals with trihydroxyglutaric acid have been studied to a limited extent. Failkov, Grigor'eva, and Davidenko [1-7] have studied the compounds of trihydroglutaric acid with iron, copper, nickel, cobalt, gallium, nd lanthanum, and have shown that the cations of trivalent elements can form electroneutral, cationic, and anionic complexes with trihydroxyglutaric acid. Davidenko [8] has studied the complex forming behavior of indium with trihydroxyglutaric acid by potentiometric titration, by measuring the electrical conductivity, and polarographically. The results of the polarographic study are only dealt with briefly in his article. The aim of our work was an all-round study of the polarographic behavior of indium over a wide pH range in the presence of a series of organic dicarboxylic acids and hydroxy acids [9], including trihydroxyglutaric acid.

EXPERIMENTAL

Indium perchlorate was prepared by dissolving indium metal in concentrated perchloric acid.

Trihydroxyglutaric acid. We used the optically inactive isomer, xylotrihydroxyglutaric acid



$$HOOC-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-COOH$$

The trihydroxyglutaric acid was recrystallized twice from water. The melting point of the acid was 137-139°. 0.5 M solutions of the acid were prepared by dissolving aliquots.

Measurements were made on a Heyrovsky automatic polarograph (galvanometer sensitivity $3.83 \cdot 10^{-9}$ amp/mm/m) at a temperature of 25 ± 0.2°. A saturated calomel electrode was used as anode. Since the waves obtained for indium in the presence of trihydroxyglutaric acid do not have maxima, there is no need to add any surface active materials.

When the acidity of the medium is changed from pH 1 to pH 4 (by addition of NaOH or $HClO_4$), indium gives well defined waves in the presence of 0.1 M trihydroxyglutaric acid. The height of the diffusion wave drops with increasing pH (Table 1); the indium wave is hardly noticeable at pH 5, while at pH 7.37 upwards it disappears completely. Nevertheless, in an alkaline medium, in the presence of excess sodium trihydroxyglutarate, indium hydroxide is not precipitated and the solution remains clear. At pH 11 a wave appears again, but at a more negative potential. The half-wave potential is shifted toward the negative side with increasing pH (Table 1, Fig. 1).

The decrease in the indium wave height with increasing pH, and also the fact that the wave even disappears between pH 7 and 11, led us to assume that indium in the form of some basic salt or hydroxide changes into a colloidal state. Using an ultramicroscope, we examined several solutions of indium in trihydroxyglutaric acid at various pH values, and found that in a $4 \cdot 10^{-4}$ M solution of indium in 0.1 M trihydroxyglutaric acid large amounts of colloidal particles could be observed. It was found that the concentration of colloidal particles is appreciably greater in solutions with pH 6, 7, 9, and 10 than in solutions with pH 2 and 3; this confirmed our assumption re the formation of a colloidal solution.

We studied the relation between $E_{\frac{1}{2}}$ of indium and the trihydroxyglutaric acid at pH 2, 3, and 4. Since the dissociation of trihydroxyglutaric acid changes with changes in the acidity of the medium, we calculated the percentage composition ofthe undissociated molecules of trihydroxyglutaric acid $[RH_2]$, as well as of uni- $[RH]^-$ and disubstituted $[R]^{2-}$ ions as a function of pH (Table 2). For these calculations we used the values of the dissociation constants of trihydroxyglutaric acid found by Grigor'eva [10], $K_1 = 5.1 \cdot 10^{-4}$ and $K_2 = 3 \cdot 10^{-5}$.

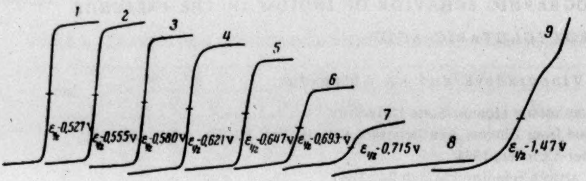


Fig. 1. The change in $E_{\frac{1}{2}}$ and in the value of the diffusion current of indium with pH, in the presence of trihydroxyglutaric acid (0.1 M) $[In^{III}] = 4 \cdot 10^{-4}$ M. 1) pH 1.62; 2) 2.33; 3) 2.99; 4) 4.02; 5) 4.41; 6) 4.88; 7) 5.45; 8) 7.36; 9) pH 11.

TABLE 1. The Relation between $E_{\frac{1}{2}}$ and the Values of the Diffusion Current and pH(in the presence of Na^+ or NH_4^+)

pH	$E_{1/2}$, b	i, мм	pH	$E_{1/2}$, b	i, мм	pH	$E_{1/2}$, b	i, мм	pH	$E_{1/2}$, b	i, мм
1,62	—0,527	53	4,02	—0,621	46	5,45	—0,715	12	~ 9	—	—
2,33	—0,555	52	4,41	—0,647	40	7,36	—	—	~10	—	—
2,99	—0,580	49	4,88	—0,693	28	~8	—	—	11	—1,47	40

TABLE 2. The Relation between $E_{\frac{1}{2}}$ and Trihydroxyglutaric Acid Concentration at pH 2, 3, and 4. $[In^{3+}] = 4 \cdot 10^{-4}$ M

pH	C_{THG}, M	C_{RH^-}, M	$C_{R_2^-}$, M	$C_{RH^-} + R^{2-}$	$E_{\frac{1}{2}}$, v
2,00	0,05	$2{,}5 \cdot 10^{-3}$	$7{,}3 \cdot 10^{-6}$		—0,548
2,10	0,07	$3{,}4 \cdot 10^{-3}$	$1{,}0 \cdot 10^{-5}$		—0,548
2,00	0,10	$4{,}9 \cdot 10^{-3}$	$1{,}5 \cdot 10^{-5}$		—0,548
2,00	0,15	$7{,}3 \cdot 10^{-3}$	$2{,}2 \cdot 10^{-5}$		—0,548
1,99	0,20	$9{,}7 \cdot 10^{-3}$	$2{,}9 \cdot 10^{-5}$		—0,548
2,01	0,30	$1{,}5 \cdot 10^{-2}$	$4{,}4 \cdot 10^{-5}$		—0,552
2,03	0,40	$1{,}9 \cdot 10^{-2}$	$5{,}8 \cdot 10^{-5}$		—0,567
3,01	0,05	$1{,}7 \cdot 10^{-2}$	$5{,}0 \cdot 10^{-4}$		—0,583
3,00	0,07	$2{,}3 \cdot 10^{-2}$	$7{,}0 \cdot 10^{-4}$		—0,583
3,02	0,10	$4{,}0 \cdot 10^{-2}$	$1{,}0 \cdot 10^{-3}$		—0,583
3,00	0,15	$5{,}0 \cdot 10^{-2}$	$1{,}5 \cdot 10^{-3}$		—0,583
2,98	0,20	$7{,}0 \cdot 10^{-2}$	$2{,}0 \cdot 10^{-3}$		—0,583
3,01	0,30	$1{,}0 \cdot 10^{-1}$	$2{,}9 \cdot 10^{-3}$		—0,590
3,00	0,40	$1{,}3 \cdot 10^{-1}$	$3{,}9 \cdot 10^{-3}$		—0,590
3,99	0,07	$4{,}7 \cdot 10^{-2}$	$1{,}4 \cdot 10^{-2}$	$6{,}0 \cdot 10^{-2}$	—0,609
4,01	0,10	$6{,}7 \cdot 10^{-2}$	$2{,}0 \cdot 10^{-2}$	$9{,}0 \cdot 10^{-2}$	—0,615
4,00	0,15	$1{,}0 \cdot 10^{-1}$	$3{,}0 \cdot 10^{-2}$	$1{,}3 \cdot 10^{-1}$	—0,622
4,00	0,20	$1{,}3 \cdot 10^{-1}$	$4{,}0 \cdot 10^{-2}$	$1{,}7 \cdot 10^{-1}$	—0,627
4,02	0,30	$2{,}1 \cdot 10^{-1}$	$6{,}1 \cdot 10^{-2}$	$2{,}6 \cdot 10^{-1}$	—0,635
4,01	0,40	$2{,}7 \cdot 10^{-1}$	$8{,}1 \cdot 10^{-2}$	$3{,}5 \cdot 10^{-1}$	—0,642

The relation between the half-wave potential and the trihydroxyglutaric acid concentration at pH 2 and ionic strength $\mu = 0.32$, at pH 3 and ionic strength $\mu = 0.12$, and also at pH 4 and $\mu = 0.32$ is given in Table 2.

At pH 2, 3, and 4 the waves have the form of waves corresponding to a reversible reduction process on the electrode. The reversibility of the process was checked on the basis of the constancy of the slope of the straight lines to the axes within the coordinates $\log(i/i_\alpha - i) - E$ and was also checked on an apparatus constructed by Sochevanov and Lyubimova [11] using Kalousek's method [12, 13] (Fig. 2). At pH 3 and 4, at a constant trihydroxyglutaric acid concentration and constant ionic strength, the value of the diffusion current is proportional to the indium concentration in solution; accordingly, indium can be determined polarographically in a supporting electrolyte of trihydroxyglutaric acid.

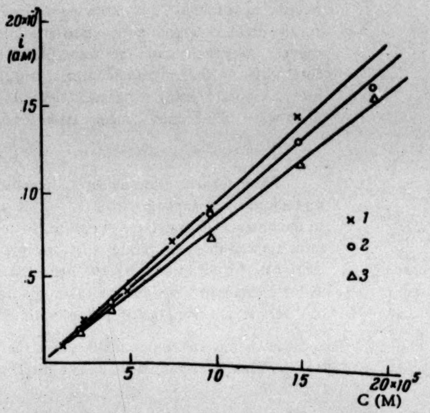


Fig. 2. Verification of the reversibility of the reduction process of indium in the presence of trihydroxyglutaric acid at pH 4 and pH 11. 1) Cathode wave at pH 4; 2) reversible anode-cathode wave of indium at pH 4; 3) cathode wave of indium at pH 11; 4) anode-cathode wave of indium at pH 11.

TABLE 3. Half-Wave Potentials of Some Elements in 0.1 M Trihydroxyglutaric Acid at pH 3*

Elements	$E_{\frac{1}{2}}$, v (relative to the saturated calomel electrode)
Tl^{I}	—0,397
Pb^{II}	—0,473
Cd^{II}	—0,662
In^{III}	—0,610
As^{III}	—0,775
Al^{IV}	Not reduced
Ga^{III}	Not reduced

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* Tin (II) and antimony (III) hydrolyze at pH 3.

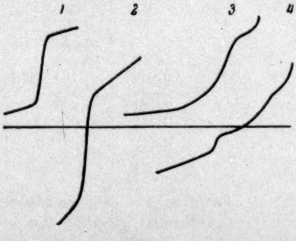


Fig. 3. Calibration curves for determination of cadmium and indium. 1) For indium at pH 3; 2) for cadmium at pH 3; 3) for cadmium at pH 9.

Although the half-wave potentials of cadmium and indium are very close in trihydroxyglutaric acid (Table 3), we have been able to develop a method for determining indium and cadmium in each others presence. According to our results, indium at pH 8 and 9 in the presence of ammonium trihydroxyglutarate does not give a wave, while cadmium under the same conditions gives a wave at a potential of −0.63 v. The solution containing a mixture of indium and cadmium salts in the presence of trihydroxyglutaric acid is adjusted to pH 3 and the total polarographic wave of indium and cadmium is taken. NH_4OH is then added to the solution until the pH is 9 (adjusted to a weak rose color of phenolphthalein) and just the cadmium wave taken. The three following calibration curves are then constructed: 1) a calibration curve for an indium solution at pH 3; 2) a calibration curve for cadmium at pH 3; 3) a calibration curve for cadmium at the same concentrations but at pH 9 (Fig. 3). From the wave height of the test cadmium solution at pH 9 and using calibration curve 3, the corresponding cadmium concentration is found. Then, knowing the cadmium concentration, the wave height for the given cadmium concentration at pH 3 is found by means of calibration curve 2. Next, the cadmium wave height thus found is subtracted from the total wave for indium and cadmium, and the wave height for indium determined. Finally, using calibration curve 1, and knowing the height of the indium wave, the indium concentration is found.

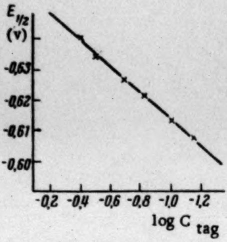


Fig. 4. The relation between $E_{\frac{1}{2}}$ for indium and the logarithm of trihydroxyglutaric acid concentration at pH 4. $[In^{III}] = 4 \cdot 10^{-4}$ M; $\mu = 0.32$.

Results of such determinations are given in Table 4.

In an alkaline medium in the presence of trihydroxyglutarate at pH 11, an indium wave appears with $E_{\frac{1}{2}} = -1.47$ v. Under the same conditions, but in the absence of trihydroxyglutarate, indium hydroxide immediately precipitates out and this precipitate only dissolves in 5 N NaOH. The half-wave potential in this solution is −1.17 v; this led us to assume that the indium wave which appears in trihydroxyglutarate and which has $E_{\frac{1}{2}} = -1.47$ v, is the wave of a very stable complex of indium with trihydroxyglutarate.

A change in the concentration of the trihydroxyglutarate anion in a strongly alkaline medium leads to a displacement of the half-wave potential (Table 5).

We examined the effect of a further increase in NaOH concentration on the nature of the reduction of indium, and found that on changing the NaOH concentration from 0.5 M to 5.0 M the half-wave potential does not alter. The wave height decreases to some extent with increasing alkali concentration; this is caused by an increase in the viscosity of the solution.

TABLE 4. Polarographic Determination of Indium and Cadmium in Each Others Presence

Taken, mg		Ratio by wt.	Found, mg		Error, %	
In	Cd		In	Cd	In	Cd
0,065	0,065	1 : 1	0,061	0,064	—6,1	—1,5
0,108	0,109	1 : 1	0,103	0,111	—4,5	+1,8
0,076	0,153	1 : 2	0,074	0,142	—2,6	—7,2
0,043	0,174	1 : 4	0,041	0,170	—4,7	—2,3
0,162	0,109	1,5 : 1	0,165	0,102	+1,9	—6,4
0,135	0,031	4,5 : 1	0,125	0,031	+7,4	±0,0
0,270	0,031	9 : 1	0,251	0,031	—7,0	±0,0
2,700	0,031	90 : 1	2,540	0,031	—5,9	±0,0

TABLE 5. The Relation between $E_{\frac{1}{2}}$ and Trihydroxyglutaric Acid Concentration in 1 N NaOH and at $\mu = 1.8$

C_{THG}, M	$C_{R^{2-}}$, M	$E_{\frac{1}{2}}$	C_{THG}, M	$C_{R^{2-}}$, M	$E_{\frac{1}{2}}$
0,40	0,40	—1,50	0,10	0,10	—1,47
0,20	0,20	—1,49	0,05	0,05	—1,46

In 1 N NaOH, for a trihydroxyglutaric acid concentration of 0.1 M and at an ionic strength of $\mu = 1.1$, the linear relation between the value of the diffusion current and indium concentration is preserved; indium can therefore be determined in such a supporting electrolyte.

Nevertheless, the half-wave potentials of some ions in a supporting electrolyte of 0.1 M trihydroxyglutaric acid and 1 N NaOH (Table 6) show that determination of indium in the presence of trihydroxyglutaric acid in a strongly alkaline medium does not have any advantages.

DISCUSSION

A regular displacement of the half-wave potential $E_{\frac{1}{2}}$ of indium with changes in trihydroxyglutaric acid concentration is only observed at pH 4 (Table 2). A small displacement of the half-wave potential at pH 2 and 3 is only observed at trihydroxyglutaric acid concentrations in excess of 0.2 M, 500 and more times greater than the indium concentration. It can be assumed that at pH 2 and 3 a very strongly dissociating complex of indium with trihydroxyglutaric acid is formed.

TABLE 6. Half-Wave Potentials of Some Ions in a 0.1 M Trihydroxyglutaric Acid Solution in 1 N NaOH

Ions	$E_{\frac{1}{2}}$ (first wave), v relative to the saturated calomel electrode	$E_{\frac{1}{2}}$ (second wave), v	Ions	$E_{\frac{1}{2}}$ (first wave), v relative to the saturated calomel electrode	$E_{\frac{1}{2}}$ (second wave), v
In^{III}	—1,47		Sn^{II}	—0,77	
Zn^{II}	—1,47		As^{III}	—1,36	
Pb^{III}	—0,77		Al^{III}	—1,42	
Tl^{I}	—0,47		Ga^{III}	Not reduced	
Sb^{III}	—1,31		Gd^{II}	—0,80	—1,30

At pH 4, $E_{\frac{1}{2}}$ is shifted toward negative potentials with increasing trihydroxyglutaric acid concentration.

At pH 4 the concentration of RH^- ions only increases insignificantly, but the concentration of R^{2-} ions increases by more than one order. On the basis of these facts one can conclude that the stable complexes which lead to an appreciable shift in $E_{\frac{1}{2}}$ are formed from indium and the R^{2-} ions of trihydroxyglutaric acid and not from indium with the RH^- ions and even less so with undissociated molecules of the acid. This conclusion agrees with Davidenko's results [8]. The relationship between the changes in $E_{\frac{1}{2}}$ with changes in trihydroxyglutaric acid concentration at pH 4 is illustrated by the straight line in Fig. 4. The coordination number P which we calculated at pH 4 was 2.1.

$$P = \frac{\Delta E_{1/2}\cdot n}{\Delta \lg C_x \cdot 0{,}059} = \frac{0{,}0265\times 3}{0{,}62\times 0{,}059} = 2{,}1.$$

Davidenko [8] gives results for the relationship between $E_{\frac{1}{2}}$ and trihydroxyglutaric acid at pH 1.5. He concludes that "the shift in potential corresponds to formation of a 1 : 1 compound." We do not think that this is quite correct. According to his results, the relationship between $E_{\frac{1}{2}}$ and the logarithm of trihydroxyglutaric acid concentration is not expressed by a straight line, but by an arc-shaped curve. By meaning the results one can produce a straight line with any slope. It would seem to us that the linear relationship is most clearly expressed for trihydroxyglutaric acid concentrations of 0.4, 0.6, and 0.8 M. On the basis of these results the value calculated for the coordination number is approximately 2.3 and not 1:

$$P = \frac{0{,}014\cdot 3}{0{,}3\cdot 0{,}059} = 2{,}3$$

and, consequently, the potential shift corresponds to a compound with a molar ratio of 1 : 2, in agreement with our results for the compound formed at pH 4.

In order to calculate the instability constant of the complex indium ion it is necessary to know the half-wave potential of the simple indium ion, e.g., in a $HClO_4$ medium. Since reduction of In^{3+} in $HClO_4$ is an irreversible process, we adopted the method of amalgam polarography.

Using an electrode in the form of a stationary drop of indium amalgam, we determined the half-peak potential during anodic dissolution of indium from the amalgam in a supporting electrolyte of 0.1 M $HClO_4$, and found it to be equal to −0.488 v. The value which we found agrees with the value of $E_{\frac{1}{2}}$ found by Cozzi and Raspi [14] by extrapolation (−0.485 ± 0.002 v).

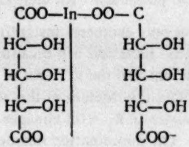
Table 7 contains results of the calculation of the instability constant, taking into account only the concentration of the doubly charged anions $C = C_{R^{--}}$. On taking into account the sum of uni- and dicharged ions $C_x - C_{R^{-}} + {}_{RH^{-}}$ the mean value of $K = (1{,}87 \pm 0{,}11) \cdot 10^{-9}$.

TABLE 7. Values of the Instability Constant of the Complex of Indium with Trihydroxyglutaric Acid

Concentration C_x, M	$E_{\frac{1}{2}}$, v	log K	pK	K
0,061	−0,635	−10,05	10,05	$8{,}91 \times 10^{-11}$
0,040	−0,627	−10,00	10,00	$1{,}00 \times 10^{-10}$
0,030	−0,622	−10,00	10,00	$1{,}00 \times 10^{-10}$
0,020	−0,615	−10,00	10,00	$1{,}00 \times 10^{-10}$

K (mean) = $(9{,}73 \pm 0{,}82) \times 10^{-11}$.

The charge of the complex of indium with 0.1 N trihydroxyglutaric acid at pH 4, as an electrophoresis method showed [1], was negative. Our experiments did not confirm Davidenko's assertion that neutral indium complexes should be present in a weakly acid medium. Bearing in mind the value p = 2, and the negative charge of the complex compound, one can assume that under our conditions In^{III} gives a complex compound of the following structure with trihydroxyglutaric acid:



In an alkaline medium (pH 11) in the presence of trihydroxyglutarate, indium forms a stable complex compound with $E_{\frac{1}{2}} = -1.47$ v. It is possible that indium is connected to the hydroxyl ions in this compound. The polarogram obtained by Kalousek's method (Fig. 3) shows that reduction of indium in the presence of trihydroxyglutaric acid in an alkaline medium is an irreversible process. We were unable to therefore to determine the coordination number polarographically and to determine the instability constant of this complex compound.

SUMMARY

The polarographic behavior of indium in the presence of trihydroxyglutaric acid has been examined in acid, neutral, and alkaline media.

The value of the half-wave potential of the simple indium ion in $HClO_4$ has been determined by measuring the value of the half-peak potential during anodic dissolution of indium from an amalgam. The half-wave potential was found to be −0.488 v.

The effect of trihydroxyglutaric acid concentration on $E_{\frac{1}{2}}$ for indium has been examined; it has been found that regular displacement of $E_{\frac{1}{2}}$ with changes in trihydroxyglutaric acid concentration is only observed at pH 4 and pH 11. It has been established that the coordination number p = 2, while it has been found that the instability constant of the complex compound formed between indium and trihydroxyglutaric acid at pH 4 has a value K (mean) = $= (9.73 \pm 0.82) \cdot 10^{-11}$.

It has been established that reduction of indium at pH 11 is an irreversible process.

A method is suggested for the polarographic determination of indium and cadmium in each others presence by using trihydroxyglutaric acid as supporting electrolyte at pH 3 and pH 9.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 18. THE THIOOXINATES OF GALLIUM, INDIUM, AND THALLIUM PHOTOMETRIC DETERMINATION OF INDIUM WITH THIOOXINE*

Yu. A. Bankovskii, Ya. A. Tsirule, and A. F. Ievin'sh

Institute of Chemistry, Academy of Sciences Latvian SSR, Riga

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The analytical chemistry of gallium, indium, and thallium has still not been developed sufficiently well. This is particularly true of methods of separating and determining gallium and indium [1]. Accordingly, the synthesis of new complex compounds, and the search for more selective reagents for these elements is of great practical importance.

As a result of studies of the analytical properties of 8-mercaptoquinoline (thiooxine) we have found that under certain conditions this reagent permits determination of microgram amounts of indium in the presence of overwhelming amounts of certain elements which usually interfere with the determination of this element by other methods.

Preparation and composition of gallium, indium, and thallium thiooxinates. Gallium salts in very weakly acid, neutral, and alkaline solutions form with thiooxine an amorphous looking orange-yellow precipitate. It can be obtained in a crystalline state from hot aqueous-alcoholic solutions. A hot solution of 0.12 g of gallium trichloride in 25 ml of 65% ethanol is added dropwise and with stirring to a filtered solution of 1.1 g sodium thiooxinate in 55 ml of 90% ethanol which has been heated to the boil. When the solutions are poured together the mixture acquires a dark-red color and an orange-yellow, crystalline precipitate of gallium thiooxinate rapidly settles out. The precipitate is filtered off through a glass filter crucible, washed several times with ethanol, and dried in air. After recrystallization from dimethylformamide the precipitate has the following composition:

Found %: Ga 12.44; N 7.50; S 17.63. $Ga(C_6H_6NS)_3$. Calculated %: Ga 12.67; N 7.64; S 17.47.

Indium salts in weakly acid, neutral, and alkaline solutions interact with thiooxine to form a yellow, amorphous looking precipitate. The precipitate can be obtained in a crystalline form from hot aqueous-alcoholic solutions. A hot solution of 0.12 g of indium trichloride in 30 ml of 40% ethanol is added dropwise and with stirring to a filtered solution of 1 g of sodium thiooxinate in 40 ml of 80% ethanol which has been heated to the boil. The yellow, crystalline precipitate which gradually settles out is filtered off through a glass crucible, washed several times with hot alcohol, and dried in air. On recrystallization from dimethylformamide the preparation has the following composition:

Found %: N 7.17; S 16.26; H 3.26. $In(C_9H_6NS)_3$. Calculated %: N 7.05; S 16.50; S 3.04.

It does not contain water of crystallization.

It has been shown earlier [2, 3] that trivalent thallium is reduced by thiooxine to its univalent state with formation of thallium (I) thiooxinate. Thallous thiooxinate can be prepared in the crystalline state from aqueous-pyridine solutions. A hot solution of 1.3 g of CH_3COOTl in 5 ml of pyridine is added dropwise to a solution of 4 g of sodium thiooxinate in a mixture of 5 ml of water and 25 ml of pyridine heated to the boil. The orange crystalline precipitate which settles out is removed by suction on a filter, washed several times with methanol, and dried in air.

Thallous thiooxinate can also be prepared in a crystalline state from ethanol-water media as in the case of gallium thiooxinate.

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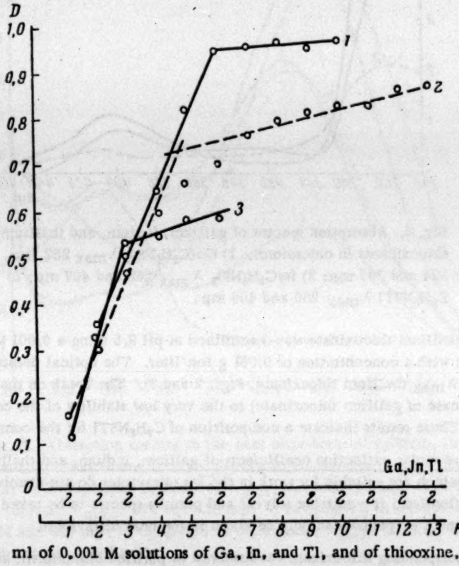
* For communication 17, see Zh. analit. khimii 16, 150 (1961).

Found %: N 3.80; S 8.75; H 1.69. $C_9H_6NS\text{-}Tl$. Calculated %: N 3.84; S 8.78; H 1.64.

Determination of active hydrogen in the preparation dried at 150° showed the absence of water of crystallization.

During measurements of the molar extinction coefficients of solutions of the thiooxinates of various elements, a feature which attracted attention was the too low molar extinction coefficient of gallium thiooxinate compared with the molar extinction coefficients of the other thiooxinates of trivalent elements and elements containing three molecules of thiooxine in the molecule. These depressed values of the molar extinction coefficients are observed both in solutions of the crystalline samples of gallium thiooxinate, and in solutions obtained by extraction from the aqueous phase. It was natural to assume that the gallium thiooxinate formed in solution is not identical to the crystalline thiooxinate. In this connection therefore we determined the composition of thiooxinates in solution. The low molar extinction coefficient of crystalline gallium thiooxinate, however, remained incomprehensible, since there was no doubt about the accuracy of the analyses of the crystalline samples. Repeated analyses of various preparations always gave results corresponding to the formula $Ga(C_9H_6NS)_3$. The reason for this low value of the molar extinction coefficient of solutions of gallium thiooxinate became apparent on studying the absorption spectra.



ml of 0.001 M solutions of Ga, In, and Tl, and of thiooxine, (R)

Fig. 1. Composition of gallium, indium, and thallium thiooxinates in a toluene extract. 1) Indium thiooxinate; 2) gallium thiooxinate; 3) thallium thiooxinate.

The composition of the thiooxinates in solution was determined by the isomolar series method. Forty ml of a borate buffer solution with pH 8 was introduced into a separating funnel; varying amounts of a 0.001 M solution of sodium thiooxinate (ml) which were gradually increased from experiment to experiment and a constant amount (ml) of a 0.001 g ion/liter solution of gallium were then added. The gallium thiooxinate formed was extracted with 20 ml of chloroform for 3 min. The chloroform extract was transferred to a 1 cm cell, and its optical density measured on a SFD-1 spectrophotometer at 397 mμ (λ_{max} of gallium thiooxinate, Figs. 2 and 3). The reference solution was a chloroform extract obtained on using the same amounts of reagents but omitting gallium. As is evident from Fig. 1, there is a break which is not sharp at Ga : R = 1 : 2, which testifies to the formation of a complex of the composition

$Ga(C_9H_6NS)_2Cl$ with low stability, or, bearing in mind its reasonably good solubility in a series of organic solvents, to the formation of a basic thiooxinate $Ga(C_9H_6NS)_2OH$, since the reaction was carried out in an alkaline medium.

The composition of indium thiooxinate was determined by the same method. To various amounts (ml of 0.001 M sodium thiooxinate at pH 7 which were increased from experiment to experiment was added a constant amount (ml) of an indium solution with a concentration of 0.001 g · ion/liter. The indium thiooxinate formed was extracted with 20 ml of chloroform, and its optical density on a SFD-1 spectrophotometer at 407 mμ (λ_{max} of indium thiooxinate, Figs. 2 and 3). The reference solution was a chloroform extract obtained on using the same amounts of reagents but omitting indium. Figure 1 shows that the sharp break on the curve corresponds to a composition of $In(C_9H_6NS)_3$ for indium thiooxinate.

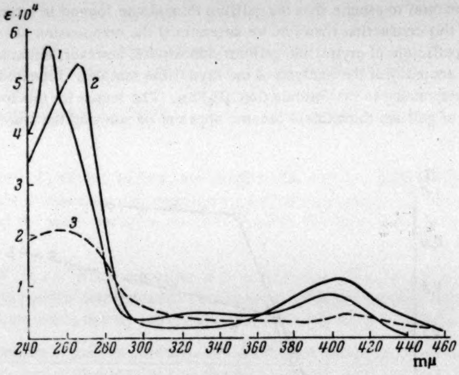
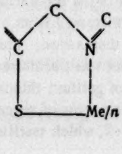


Fig. 2. Absorption spectra of gallium, indium, and thallium thiooxinates in chloroform. 1) $Ga(C_9H_6NS)_3$ λ_{max} 252 mμ, 324 and 397 mμ; 2) $In(C_9H_6NS)_3$ λ_{max} 268 and 407 mμ; 3) C_9H_6NSTl λ_{max} 250 and 406 mμ.

The composition of thallium thiooxinate was determined at pH 9.5 using a 0.001 M solution of thiooxine and a solution of a thallous salt with a concentration of 0.001 g ion/liter. The optical density of the chloroform extract was measured at 406 mμ (λ_{max} thallium thiooxinate, Figs. 2 and 3). The break on the curve which is not sharp (Fig. 1) testifies (as in the case of gallium thiooxinate) to the very low stability of the complex found between Tl : R = = 1 : 1 and Tl : r = 1 : 1/3. These results indicate a composition of C_9H_6NSTl for the complex.

Absorption spectra and molar extinction coefficients of gallium, indium, and thallium. As the data in Table 1 show, most of the solvents which are suitable for work in the far ultraviolet do not dissolve gallium, indium, and thallium thiooxinates. Only chloroform is a suitable solvent and permits spectra to be taken at wavelengths higher than 245 mμ. In the other solvents the spectra can only be taken in the near ultraviolet.

An aliquot of the corresponding thiooxinate was dissolved in purified chloroform, and the optical density measured on a SF-4 spectrophotometer relative to chloroform. As Figs. 2 and 3 show (long wave maxima at higher concentrations of the thiooxinates are shown in Fig. 3), the absorption spectra of gallium and indium thiooxinates have three maxima each, while thallium has two. The maxima in the far ultraviolet (Ga, 252 mμ; In, 268 mμ, Tl, 250 mμ) belong to the quinoline nucleus, while the maxima on the boundary of the ultraviolet and visible regions (Ga, 397 mμ; In, 407 mμ; Tl, 406 mμ) belong to the cyclic group



where Me = Ga, In, Tl; n is the valence of the element. The maximum at 324-325 mμ for gallium thiooxinate, and the weak maximum for indium thiooxinate belong to the thiooxinate ion $C_9H_6NS^-$ formed as the result of the dissociation of the molecules of the thiooxinates:

$$Ga(C_9H_6NS)_3 \rightarrow Ga(C_9H_6NS)_2^+ + C_9H_6NS^-$$

$$In(C_9H_6NS)_3 \rightarrow In(C_9H_6NS)_2^+ + C_9H_6NS^-$$

This is quite clear from the absorption spectrum of sodium thiooxinate in ethanol (Fig. 3, curve 6), the absorption maximum of which at 324-325 mμ corresponds with the absorption maxima of gallium and indium thiooxinates in chloroform.

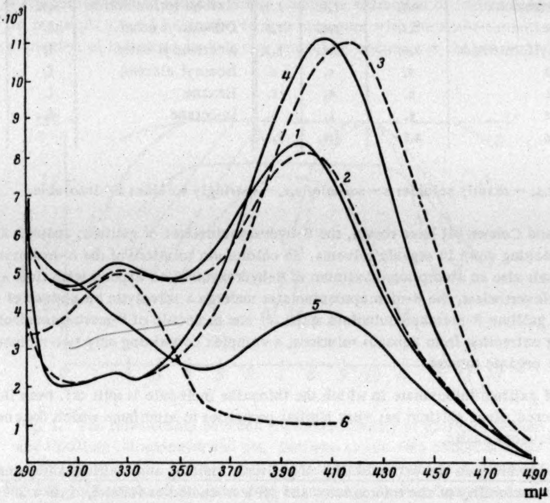


Fig. 3. Absorption spectra in the near ultraviolet of gallium, indium, and thallium thiooxinates. 1) $Ga(C_9H_6NS)_3$ in chloroform; λ$_{max}$, 324 and 397 mμ; 2) $Ga(C_9H_6NS)_3$ in toluene, λ$_{max}$, 324 and 400 mμ; 3) $In(C_9H_6NS)_3$ in toluene; λ$_{max}$, 324 and 418 mμ; 4) $In(C_9H_6NS)_3$ in chloroform; λ$_{max}$, 324 and 407 mμ; 5) C_9H_6NSTl in chloroform; λ$_{max}$, 406 mμ; 6) sodium thiooxinate in ethanol.

Solutions of the crystalline thiooxinates in purified chloroform were prepared in order to determine the molar extinction coefficients. The optical density of the solutions was measured relative to chloroform on a SF-4 spectrophotometer at the absorption maxima of the thiooxinates. The mean values of the molar extinction coefficients, obtained from many experiments at different concentrations of the thiooxinates in chloroform, were as follows: gallium thiooxinate $Ga(C_9H_6NS)_3$ – ε = 8400; indium thiooxinate $In(C_9H_6NS)_3$ – ε = 11,100; thallium thiooxinates C_9H_6NS-Tl approximately 4000. The type of solvent used has almost no effect on the value of the molar extinction coefficient.

The values of the extinction coefficients of the thiooxinates are approximately proportional to the amount of combined molecules of thiooxinate. In particular, the molar extinction coefficients of the thiooxinates into whose composition three molecules of thiooxine enter, are approximately 12,000. In such a case the molar extinction coefficients of $Ga(C_9H_6NS)_3$ and $In(C_9H_6NS)_3$, as long as their composition remains unchanged should also be equal to about 12,000. From this point of view, the molar extinction coefficient of indium thiooxinate is slightly low, while the molar extinction coefficient of gallium thiooxinate corresponds to that of a thooxinate containing only two molecules of thiooxine. This is in good agreement with the interpretation advanced above of the absorption spectra and to the equations for the dissociation of thiooxinates.

TABLE 1. Solubility of the Crystalline Thiooxinates of Gallium, Indium, and Thallium in Organic Solvents

Solvent	Thiooxinate			Solvent	Thiooxinate		
	Ga	In	Tl		Ga	In	Tl
Chloroform	r.s.	r.s.	s.	Ethanol	i.	i.	i.
Bromoform	r.s.	r.s.	r.s.	Nonyl alcohol	i.	i.	i.
Bromobenzene	r.s.	r.s.	r.s.	Carbon tetrachloride	s.s.	s.s.	s.s.
Pyridine	r.s.	r.s.	r.s.	Diisoamyl ether	i.	i.	i.
Dimethylformamide	r.s.	r.s.	r.s.	Acetoamyl ester	i.	i.	i.
Toluene	s.	s.	s.	Isoamyl alcohol	i.	i.	i.
Benzene	s.	s.	s.	Hexane	i.	i.	i.
Acetone	s.	s.	s.	Isooctane	i.	i.	i.
Dioxane	s.s.	s.s.	s.s.				

Notes: r.s. — readily soluble; s — soluble; s.s. — sparingly soluble; i — insoluble.

As Moeller and Cohnen [4] have shown, the 8-hydroxyquinolates of gallium, indium, and thallium also possess this capacity of breaking down in organic solvents. In chloroform solutions of the 8-hydroxyquinolates of gallium, indium, and thallium also an absorption maximum of 8-hydroxyqinoline appears with time as in the case of 8-mercaptoquinolates. Nevertheless, the 8-mercaptoquinolates undergo a solvolytic breakdown of this kind appreciably more rapidly; thus gallium 8-mercaptoquinolate splits off one molecule of 8-mercaptoquinoline almost instantaneously, while during extraction from aqueous solutions, a complex containing only two molecules of 8-mercaptoquinoline passes into the organic solvent.

Breakdown of gallium thiooxinate in which the thiooxine molecule is split off, even in an organic solvent medium, is not unexpected, since gallium has very similar properties to aluminum which does not in general form a salt with thiooxine in aqueous media.

The relationship between the extractability of gallium, indium, and thallium thiooxinates and pH. The relationship between the extractability of the thiooxinates and pH was studied as follows. Into a 200 ml separating funnel containing 30-40 ml of a buffer solution with the requisite pH was introduced the requisite amount (theoretical number of moles with respect to the element Ga(In): R = 1 : 3 and Tl : R = 1 : 1, or an excess number of moles) of sodium thiooxinate in the form of an aqueous solution; the solution of the test element was then added. When the theoretical amount of thiooxine was used, indium and thiooxine solutions with a concentration of 0.001 g ion/liter were used. When excess thiooxine was used, its concentration was increased. In order to ensure identical experimental conditions the total volume after mixing the solutions was 50 ml in each case. The thiooxinate formed was extracted for 3 min with 10 ml toluene. The toluene extract was filtered free from drops of water by passing it through a plug of cotton wool, and its optical density measured in a 1 cm cell on a FEK-N-54 photocolorimeter fitted with a violet filter. As Fig. 4 shows, the thiooxine concentration affects the range over which the thiooxinates can be extracted. When the theoretical amount of thiooxine is used (Ga : R = 1 : 30, even when the maximum amount of complex is formed at pH about 7) the extractability does not reach 100%. When a ten-fold excess of reagent is used, gallium thiooxinate is extracted over the range pH 6.5-10, while for a 100-fold excess of reagent it is extracted over the range pH 5.5-10. Further increases in the thiooxine concentration do not essentially affect completeness of extraction of gallium, particularly in acid solutions.

Thiooxine concentration affects the extrability of indium in the same way: when the theoretical amount of reagent is used (In : r = 1 : 3) only about 83% indium is extracted over the range pH 4-10, while when a ten-fold excess of reagent is used 100% extractability is observed over the range pH 4-13. Further increases in thiooxine concentration slowly extend the region over which indium thiooxinate is stable.

Figure 4 shows that thallium thiooxinate is only stable in alkaline solutions. When the theoretical amount of reagent is used, thallium is 100% extracted over the range pH 10-14, while for a ten-fold and 100-fold excess of reagent the corresponding pH ranges are 9-14, and 7.5-14.

Of considerable interest is a comparison of the relative stability of the 8-hydroxyquinolates and thiooxinates of gallium, indium, and thallium. Since the dissociation constants of gallium, indium, and thallium have not hitherto been determined, in order to have an approximate comparison, use can be made of the extractability ranges of the oxinates and thiooxinates. The following results are given in the literature. Lacroix [5] is of the opinion that extraction of gallium 8-hydroxyquinolate starts to be quantitative from pH 2. Lacroix's experiments, however, were only approximate. Sandell [6] has stated that quantitative extraction of gallium 8-hydroxyquinolate occurs over the pH range 2.6-3.0. According to other results [7], extraction of gallium 8-hydroxyqinolate is quantitative over the pH range 3.0-6.2.

Moeller [8] has found that the range over which indium 8-hydroxyquinolate is extracted quantitatively is pH 3.2-4.5. Milner [9] is of the opinion that in order to ensure complete extraction of indium 8-hydroxyquinolate, it is necessary to work in the range pH 3.5-4.5. Lacroix [5] does not agree with the authors mentioned above and considers that quantitative extraction of indium as its 8-hydroxyquinolate occurs over the pH range 3-5.

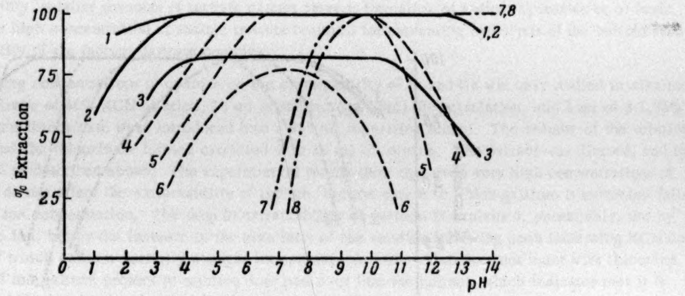


Fig. 4. The relationship between the extractability of gallium, indium, and thallium thiooxinates and pH. Indium: 1) 100-fold excess of thiooxine (R); 2) ten-fold excess of R; 3) theoretical amount of R; gallium: 4) 100-fold excess of R; 5) ten-fold excess of R; 6) theoretical amount of R; thallium: 7) ten-fold excess of R; 8) theoretical amount of R.

Apart from the disagreement between the results of different authors, another noteworthy feature is that the range of extraction of the 8-hydroxyquinolates of Ga and In is limited to weakly acid solutions and does not extend to the alkaline region as is the case for thiooxinates. The reason for this is that the authors mentioned above were interested in the extractability range for practical purposes, and, in this connection adjusted the requisite pH in the metal solution first and only then added 8-hydroxyqinoline. The consequence of this would be that the basic salts formed in weakly acid solutions, or the hydroxides formed in alkaline solutions, will not react with 8-hydroxyqinoline. The order in which the reagents are mixed has an essential effect on the extraction range (formation) of the complex salt.

To avoid this when working with thiooxine, as is evident from the technique described above, we added the solution of the test element dropwise to the buffered solution of thiooxine. Thus in the case of alkaline solutions we determined the relative rate of hydrolysis and formation of the thiooxinate. Moreover, in order to obtain comparable results, it is essential to determine the extractability range of the 8-hydroxyquinolates and thiooxinates under strictly analogous conditions — buffer solutions of the same composition and equal concentrations of reagents (8-hydroxyquinoline and thiooxine). In this connection we determined the extractability range of gallium and indium 8-hydroxyquinolates by the same method as that described above for thiooxinates, using a ten-fold excess of 8-hydroxyquinoline over that theoretically necessary for formation of the complex Me(Ox)$_3$. Gallium 8-hydroxyquinolate is extracted quantitatively over the range pH 5-13 (Fig. 5). It follows from these results that indium thiooxinate (pH 4-13) is more stable than indium 8-hydroxyquinolate. Gallium 8-hydroxyquinolate, on the other hand is more stable than gallium thiooxinate (pH 6.5-10).

Bearing in mind the strong alkaline properties and the ready solubility in water of thallous hydroxide, one might expect that thallous 8-hydroxyquinolate will have low stability; this is confirmed by Moeller and Cohnen's work [10]. On the other hand, taking into account the poor solubility of Tl_2S, one might assume that its thiooxinate will have a relatively high stability. Actually, while Moeller and Cohnen [10] were only able to precipitate 0.87 g of thallium from 1 g of thallium in an alkaline medium with 8-hydroxyquinoline, using thiooxine, as can be seen from Fig. 4, it should be possible to extract microgram amounts of thallium quantitatively over the range pH 9-14.

Thus if one assumes that the stability of the bond Me(Ga, In, Tl)-N does not change in the 8-hydroxyquinolates and thiooxinates, one must conclude that the bond Ga—O is more stable than the bond Ga—S, while the reverse is true in the case of indium and thallium: the bonds In—S and Tl—S are more stable than the bonds In—O and Tl—O.

When a ten-fold excess of thiooxine is used over that theoretically necessary for formation of $In(C_9H_6NS)_3$, indium thiooxinate is extracted over the range pH 4-13. The wide range over which indium can be extracted permits one to determine this element both in weakly acid and in alkaline solutions. Determination of indium in weakly acid solutions does not have any practical importance, since most elements which form sulfides which are stable in aqueous media interact with thiooxine in weakly acid media. KSCN, KI, $CS(NH_2)_2$, KF, citrate, oxalate, thiosulfate, pyrophosphate, and sodium ethylenediaminetetracetate proved unsuitable for masking foreign elements in acid media.

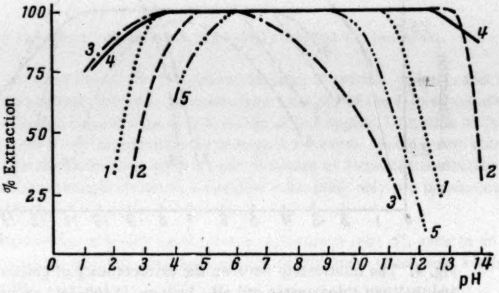


Fig. 5. The relationship between the extractability of gallium (1) and indium (2) 8-hydroxyquinolates and the pH of the medium (order in which the components were mixed: buffer + 8-hydroxyquinoline + metal). The relationship between the extractability of indium thiooxinate and the pH of the medium (3); order in which the components were mixed: indium + buffer + thiooxine. Effect of tartrate ions (14% solution of sodium tartrate) on the extractability range of indium (4) and gallium (5) thiooxinates.

Effect of cyanide and tartrate ions on completeness of extraction of indium and gallium thiooxinates. The pH range over which indium is extracted as its thiooxinate (pH 4-13) and which was found above, is only valid when an indium solution is added to a solution of thiooxine in a buffer medium with a definite pH. In actual practice one usually proceeds otherwise: the pH of the solution is established at the requisite value first and the reagent solution then added. When such a technique is adopted, in alkaline solutions hydroxides of basic salts of indium are formed which only partially interact with the thiooxine. Figure 5 shows the extractability curve of indium obtained by the method described above, but with the components mixed in the reverse order. As Fig. 5 shows, extraction of indium is quantitative only over the range pH 3.5-6. Formation of basic salts or hydroxides of indium can be prevented by addition of sodium tartrate, which is also necessary for keeping other metals in solution in an alkaline medium. The effect of the tartrate ion on the extractability range was examined as follows. Thirty-five ml of a 20% solution of neutral sodium tartrate and 10 ml (30 μg) of a solution of an indium (gallium) salt were introduced into a 200 ml separating funnel. The pH was adjusted to the requisite value by means of NaOH or HCl solutions and the volume of the solution made up to 50 ml with water. One ml of a 1.25% solution of sodium thiooxinate at the same pH was then added. The thiooxinate formed was extracted by vigorous shaking with 10 ml of toluene. The extract was filtered through a plug of cotton wool and its optical density measured in a 1 cm cell on a FEK-N-54 photocolorimeter fitted with a violet filter. Pure toluene was used as the reference solution. The amount of indium (gallium) present was determined by means of a calibration curve constructed under conditions ensuring maximum extractability of the given thiooxinate, but without tartrate.

As Fig. 5 shows, in the presence of tartrate ions, indium is extracted over the range pH 4-12.5, while gallium is extracted over the range pH 6-10. These ranges coincide with the extractability ranges determined earlier under conditions which exclude hydrolysis of indium and gallium salts. This confirms the explanation given above for the very narrow extraction range for indium when no tartrate is used and when thiooxine is added after buffering the indium solution.

The effect of sodium tartrate concentration on the completeness of indium extraction was studied by the technique described above. The only difference in the experimental conditions was that the reaction was carried out in a buffer solution with pH 11, and that the amount of 20% sodium tartrate solution added was varied from experiment to experiment. It follows from these experiments that at pH 11, and for a total volume of 50 ml of solution, a minimum amount of 8 ml of 20% sodium tartrate solution is necessary for ensuring quantitative extraction of indium as its thiooxinate. Presumably, smaller amounts of tartrate cannot prevent formation of indium hydroxide or of basic indium salts. The rather high concentration of sodium tartrate required for preventing hydrolysis of the indium salts testifies to the low stability of the indium-tartrate complex.

The effect of varying concentrations of cyanide on the extractability of In and Ga was only studied in alkaline solutions. A definite volume of 40% KCN solution, 10 ml of indium (gallium) (30 μg) solution, and 1 ml of a 1.25% aqueous solution of sodium thiooxinate were introduced into a 200 ml separating funnel. The volume of the solution was made up to 50 ml and the thiooxinate formed extracted with 10 ml of toluene. The extract was filtered, and its optical density measured as described above. The experimental results show that even very high concentrations of cyanide ions in solution do not affect the extractability of indium, but the extent to which gallium is extracted falls with increasing cyanide ion concentration. The drop in extractability of gallium is explained, presumably, not by the effect of the cyanide ion, but by the increase in the alkalinity of the solution following upon increasing KCN concentration, as a result of which gallium partially changes into an anionic form which does not react with thiooxine. Nevertheless, the bulk of the gallium present in solution does pass over into the extract, which indicates that it is impossible to determine indium in the presence of gallium by means of thiooxine.

These experiments show that cyanide ions do not form an appreciably stable complex with indium. But, as the technique described above shows, the experiments on the study of the effect of cyanide on the extractability of indium in a strongly alkaline medium were carried out without tartrate; nevertheless, indium was extracted completely in the form of the compound $In(C_9H_6NS)_3$. This indicates that cyanide ions form some sort of complex of low stability with indium, which prevents formation of indium hydroxide which does not react with thiooxine.

Thus indium can be photometrically determined in the presence of KCN and tartrate, but gallium cannot be determined in this way. In this connection we have examined the effect of thiooxine concentration on the extractability of indium in the presence of 20 ml of 40% KCN solution. The amount of indium taken, and the whole experimental procedure were identical to those described above. Only the concentration of sodium thiooxinate in the test solution was varied from experiment to experiment. These experiments show that five times the theoretical amount of thiooxine necessary for formation of $In(C_9H_6NS)_3$ should be used for ensuring quantitative extraction of indium. Further increases in thiooxine concentration do not affect the extractability of indium.

The sensitivity of the reaction and conformation of solutions of indium thiooxinate to Beer's law. A calibration curve was constructed by introducing 10 ml of 20% sodium tartrate, and 20 ml of 40% KCN solution into a 200 ml separating funnel; these were followed by various amounts of a solution of an indium salt and 1 ml of 1.25% sodium thiooxinate solution, the volume of the aqueous phase being finally made up to 50 ml. The indium thiooxinate was extracted by vigorous shaking for 3 min with 10 ml of toluene. After filtration through a plug of cotton wool, the optical density of the extract was measured in a 1 cm cell on a spectrophotometer at 407 mμ or on a photocolorimeter with a violet filter. When the FEK-N-54 photocolorimeter was used it was found that toluene solutions of indium thiooxinate confirm to Beer's law over the range 5-60 μg indium/ml. When 10 ml of toluene is used for extraction it is possible to determine as little as 0.5 μg indium, with an error of ±10%. The error decreases to 3-4% in the case of larger amounts of indium.

Indium can also be determined in a weakly acid medium at pH 5-6. The extracts obtained in an acetate buffer (without tartrate and cyanide) conform to Beer's law over the same indium concentration range. The curve is, however, somewhat higher since the isoelectric point of thiooxine is located at pH 5.1, and at this point thiooxine exhibits its lowest solubility in water and is most completely extracted with organic solvents so that a continuous supplementary background is created.

Determination of indium in the presence of other elements. In the experiments described below, which were carried out by the method used above for constructing a calibration curve (in an alkaline medium in the presence of cyanide and tartrate), 20 μg of indium was determined against a background of various amounts of foreign elements. The optical density of the toluene extracts was measured on a FEK-N-54 photocolorimeter fitted with a violet filter. The amount of indium to be determined was found from the calibration curve constructed with the aid of pure solutions of indium as described above. The results obtained are given in Table 2. KCN was used for masking Cu, Cd, Ag, Au, Co, Ni, Fe and Pt. Gold must be reduced beforehand with sodium metabisulfite at pH 5-6 to its univalent state, since Au^{III} vigorously oxidizes thiooxine to 8,8'-diquinolyldisulfide. For determination of indium in the presence of gold, 10-20 ml of the acid test solution is neutralized to pH 3-5, 4 ml of a 30% sodium acetate solution is added, followed by 5 ml of 20% sodium metabisulfite and 1 ml of a 1.25% solution of sodium thiooxinate. The procedure outlined above is then followed. It is possible to determine microgram amounts of indium in the presence of 250 mg of gold by this method.

TABLE 2. Determination of Indium in the Presence of Other Elements (20 μg In taken)

Foreign element (Me), mg	Ratio In: Me	In found, μg	Error, %	Foreign element (Me), mg	Ratio In: Me	In found, μg	Error, %
Cu^{2+} 10	1 : 500	20,5	2,5	W^{VI} 1500	1 : 75000	21	5
Cd^{2+} 1	1 : 50	19	—5	Re^{VII} 20	1 : 1000	20	0
Ag^{+} 3000	1 : 150000	20	0	Fe^{2+} 150	1 : 7500	19,5	—2,5
Au^{+} 250	1 : 12500	21	5	Co^{2+} 20	1 : 1000	20,4	2
Ge^{IV} 1200	1 : 60000	19,6	—2	Ni^{2+} 30	1 : 1500	20,5	2,5
Th^{IV} 500	1 : 25000	19,4	—3	Pd^{2+} 50	1 : 2500	20,9	4,5
V^{V} 20	1 : 1000	20	0	Pt^{IV} 100	1 : 5000	20,5	2,5
As^{V} 500	1 : 25000	20,5	2,5	Os^{VIII} 6,2	1 : 310	19,7	—1,5
Gr^{III} 140	1 : 7000	20,8	4	UO_2^{2+} 580	1 : 24000	19	—5
Mo^{VI} 1000	1 : 50000	19,6	—2				

Iron can only be bound as a fairly stable cyanide complex after reducing it to its divalent state with hydroxylamine or ascrobic acid. Other reducing agents (NaH_2PO_2, Na_2SO_3, $Na_2S_2O_4$) do not reduce iron quantitatively to Fe^{2+}, so that iron cannot be complexed completely. Two ml of a freshly prepared 20% solution of ascorbic acid (or hydroxylamine) is added to 10-20 ml of the weakly acid test solution, 2 ml of 20% sodium tartrate solution is then added, and the solution obtained neutralized with alkali to pH 8-9, 20 ml of 40% KCN solution is added and the whole boiled until the color of the solution changes to pure yellow. The procedure outlined above is then followed. Microgram amounts of indium can be determined in the presence of 120 mg iron by this method.

Other elements, in the amounts indicated in Table 1, do not introduce any difficulties into the determination of indium. Neither do any of the elements which do not form sulfides which are stable to the action of water interfere (Al, Zr, Ti, etc.).

Mn, Zn, Hg, Ga, Tl, Sn, Pb, Sb and Bi should be absent.

Anions (Cl^-, Br^-, I^-, F^-, NO_3^-, SO_4^{2-}, CH_3COO^-, ClO_4^-, $B_4O_7^{2-}$, CNS^-, PO_4^{3-}, CO_3^{2-}, $C_2O_4^{2-}$, NO_2^- citrate, tartrate, and cyanide) do not affect the accuracy of indium determination.

SUMMARY

Crystalline gallium $Ga(C_9H_6NS)_3$, indium $In(C_9H_6NS)_3$, and thallium TlC_9H_6NS thiooxinates have been synthesized. It has been established spectrophotometrically that gallium thiooxinate dissociates in organic solvents to form the ion $Ga(C_9H_6NS)_2^+$. Indium thiooxinate tends to dissociate in the same way but to a lesser extent. The values of the molar extinction coefficients of gallium thiooxinate (ε = 8400) and indium thiooxinate (ε = 11,000), measured

at the absorption maxima of the complexes, also testify to complete dissociation of gallium thiooxinate with formation of the ion $Ga(C_9H_6NS)_2^+$, and partial dissociation of indium thiooxinate with formation of the ion $In(C_9H_6NS)_2^+$. Thallium thiooxinate has a molar extinction coefficient of about 4000, which confirms the composition TlC_9H_6NS.

Indium and thallium thiooxinates have the same composition in solution in organic solvents and in the crystalline state. Gallium thiooxinate is formed at a ratio of Ga : R = 1 : 2, i.e., organic solvents apparently extract a complex of the composition $Ga(C_9H_6NS)_2$ or a basic thiooxinate $Ga(C_9H_6NS)_2OH$.

When ten times the amount of thiooxine theoretically necessary for formation of the thiooxinates is used, gallium is extracted at pH 6.5-10, indium at pH 4-13, and thallium at pH 9-14. Under similar conditions gallium 8-hydroxyquinolate is extracted at pH 3.5-11 and indium 8-hydroxyquinolate at pH 5-13.

A method has been developed for the photometric determination of indium with thiooxine (8-mercaptoquinoline). The method is based on formation of indium thiooxinate $In(C_9H_6NS)_3$ which is extracted with toluene to give a yellow colored solution. The indium complex is extracted at pH 4-12.5. From 0.5 to 60 μg of indium can be determined in 50 ml. The selectivity of the reaction is low in a weakly acid medium. It is possible to mask overwhelming amounts of Cu, Ag, Au, Fe, Co, No, Pb, and Pt by means of potassium cyanide in an alkaline medium. Ge, V, As, Mo, W, Re, U and all those elements which do not form sulfides which are stable in aqueous solution (Al, Zr, Tl, Cr, Th, etc.) do not interfere either. Mn, Zn, Hg, Ga, Tl, Sn, Pb, Sb, and Bi interfere with indium determination. The advantage of the method suggested is the possibility of determining microgram amounts of indium in the presence of overwhelming amounts of silver, gold, palladium, and platinum without preliminary removal of these elements. The thiooxine method for the determination of indium in an alkaline medium in the presence of potassium cyanide is more selective than the 8-hydroxyquinoline method.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

2,7-DICHLOROCHROMOTROPIC ACID – A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF TITANIUM

V. I. Kuznetsov and N. N. Basargin

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR, Moscow

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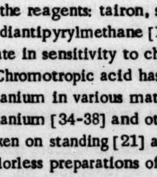
Relatively few good reagents are known for titanium. Arsenazo, thoron, and other reagents give color reactions of low contrast and selectivity with titanium. Reactions based on formation of the bond Ti–O [1] are of the greatest practical importance for titanium. Determination of titanium with hydrogen peroxide [2] is not too sensitive and selective. More sensitive are methods based on the reagents: tairon, sulfosalicylic acid [7-9], salicylic acid [9-11], pyrocatechol [5, 12, 13], ascorbic acid [14-16], diantipyrylmethane [17], salicylhydroxamic acid [18], dihydroxymaleic acid [19] etc. These reagents approximate in sensitivity to chromotropic acid [20] – one of the most sensitive of the readily available reagents for titanium. Chromotropic acid has been used for developing a number of methods of determining [21-26] and detecting [27-33] titanium in various materials, and a considerable amount of work has been devoted to studies of its complexes with titanium [34-38] and other elements [39-43]. Chromotropic acid, however, has serious disadvantages: its solutions darken on standing [21] and this process is accelerated in the presence of copper [36]; it is almost impossible to obtain colorless preparations of the reagent. Browning of aqueous solutions of chromotropic acid is related to its oxidation as a result of the high reactivity of the hydrogen atoms in positions "2" and "7." When the latter are substituted by chlorine or bromine atoms, the reagents obtained are stable to oxidation.

The present article is devoted to a description of a new organic reagent for quadrivalent titanium – 2,7-dichlorochromotropic acid – which has been synthesized by the authors, and to the possibilities of its analytical application.

Dichlorochromotropic acid exists as fine, colorless needles



which are soluble in water and sparingly soluble in ethanol. Its disodium salt crystallizes with two molecules of water; it is less soluble than the free acid, and is readily purified by recrystallization from water.

The absorption curves of solutions of disodium dichlorochromotropate are shown in Fig. 1. Aqueous solutions of this salt are colorless and hardly change at all on storing in direct sunlight. Special experiments devoted to a study of the comparative stability of 0.01 M aqueous solutions of chromotropic and dichlorochromotropic acids to hydrogen peroxide, showed that chromotropic acid darkens 400 times more quickly than dichlorochromotropic acid under such conditions.

Dichlorochromotropic acid interacts, under suitable conditions for each element, to form colored compounds with Ti^{IV} (raspberry), Fe^{III} (green), U^{VI} (brown), Hg^{II,I} (pale light-yellow), Mo^{VI}, W^{VI} (yellow), Cr^{VI} (rose-violet in almost concentrated H_2SO_4), V^{IV} (dark-green). Ce^{IV} and Mn^{VII} oxidize the reagent, as a result of which a yellow color develops.

Under the conditions used for the photometric determination of titanium, dichlorochromotropic acid does not give colors with Ag, Al, Ba, Be, Bi, Ca, Cd, Co^{II}, Cr^{III}, C^{I,II}, Fe^{II}, Ga, Hg^{I,II}, In, Mg, Mn^{II}, Ni, Pb, Pt^{IV}, Sb^{III}, Se^{VI}, Sn^{II,IV}, Sr, Te^{IV}, Th, Tl^{III}, ΣTR, Zn, Zr.

Solutions of titanium compounds have an absorption maximum at 490 mμ. Dichlorochromotropic acid reacts with Ti^{IV} in more acid media than chromotropic acid; the pH values at which the reaction proceeds to 50% extent are 0.7 and 1.8 respectively. The effect of pH on color development is shown in Fig. 2. The sensitivity of dichlorochromotropic acid for titanium at pH 1.0 is 12 times the sensitivity of the hydrogen peroxide reaction, while at pH 2.0 it is 14 times more sensitive. The comparison was made with the sensitivity of the reaction under the conditions used for determination of titanium with hydrogen peroxide [44]. The molar extinction coefficient of solutions of the compound formed between titanium and dichlorochromotropic acid is equal to $1.12 \cdot 10^4$ at pH 2.0, and $0.80 \cdot 10^4$ at pH 1.0 and λ = 490 mμ.

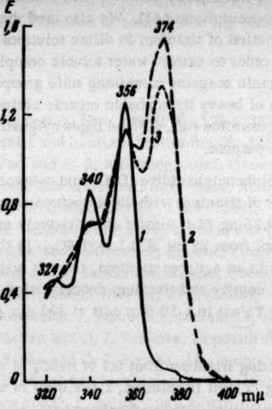


Fig. 1. Absorption curves of $1 \cdot 10^4$ M solutions of disodium dichlorochromotropate. 1) In 0.1 N H_2SO_4 (against H_2O); 2) in 0.1 N NaOH (against 0.1 N NaOH); 3) in H_2O (pH 4.1; against H_2O SF-4 spectrophotometer, 10 mm cell.

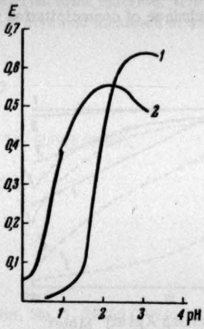


Fig. 2. Effect of pH on the development of color between Ti^{IV} and 1) chromotropic acid (λ = = 450 mμ); 2) dichlorochromotropic acid (λ = 490 mμ); concentrations: reagent, $5 \cdot 10^{-4}$ M; titanium $5 \cdot 10^{-5}$ M; SF-5 spectrophotometer, 10 mm cell.

In $7.5 \cdot 10^{-4}$ M solutions of dichlorochromotropic acid at pH 1.0, using a 10 mm cell and a wavelength of 490 mμ, 0.1 μg Ti/ml gives an extinction of 0.018. For the reagent concentration indicated the calibration line is linear up to a titanium concentration of 4-5 μg/ml. Results of the spectrophotometric determination of titanium in pure solutions are given in the table.

Spectrophotometric Determination of Titanium with Dichlorochromotropic Acid. Reagent Concentration $7.5 \cdot 10^{-4}$ M (volume of solution 10 ml, cell 10 mm, λ = 490 mμ. The optical density was measured relative to a solution of the reagent)

Ti taken, μg	Found			
	pH 1.0 (0.1 N HCl)		pH 2.0 (0.001 N HCl)	
	μg Ti	relative error, %	μg Ti	relative error, %
1	1.05	+5	1.00	0.0
5	5.05	+1	5.00	0.0
25	25.2	+ 0.8	15.0	0.0
50, 40	50.1	+ 0.2	40.0	0.0

The reaction is fairly selective at pH 1.0. Under these conditions, U^{VI}, V^{IV}, and $Hg^{II,I}$ do not interfere with titanium determination. Fe^{III}, Cr^{VI}, V^{V}, Mo^{VI}, and W^{VI} interfere strongly. Interference from Fe^{III}, V^{V}, and Cr^{VI} can be removed by reducing them with ascorbic acid, while Mo^{VI} and W^{VI} can be masked with phosphate.

The masking effect of fluorides, phosphates, tartrates, and sodium ethylenediaminetetracetate (EDTA-Na) is shown in Fig. 3. In the case of the reaction of Ti^{IV} with dichlorochromotropic acid, the effect of oxalates is almost analogous to the effect of EDTA-Na. Ascorbic acid in 100-fold excess does not mask Ti^{IV}.

Determination of small amounts of titanium in dilute solutions. In analytical practice, e.g., during hydrochemical studies, it is frequently necessary to determine microgram amounts of elements in very dilute solutions.

In such cases photometric determinations are carried out after preliminary concentration extraction, or after using the new technique of coprecipitation with colorless organic coprecipitants [45]. We also used these techniques for the determination of titanium in dilute solutions. It is known [45, 46] that in order to extract water soluble complex compounds formed with organic reagents containing sulfo groups, it is necessary to add salts of heavy hydrophobic organic cations to the solution. Diphenylguanidine [45, 46] and triphenylguanidine [47] etc., are used for this purpose.

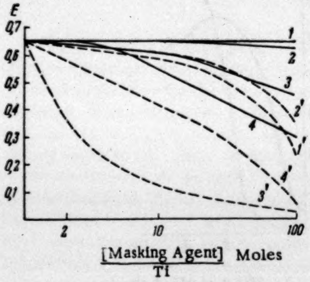


Fig. 3. Effect of tartrates (1), phosphate (2), EDTA-Na (3), and fluorides (4) on the reaction between Ti^{IV} and chromotropic acid (pH 3.0, λ = 450 mμ); and dichlorochromotropic acid)pH 1.0, λ = 490 mμ); concentrations: reagent, $7.5 \cdot 10^{-4}$ M; titanium $5 \cdot 10^{-5}$ M.

We used diphenylguanidine (DPG) and n-butanol for extracting the complex of titanium with dichlorochromotropic acid. It was found that 0.25 μg Ti is almost quantitatively extracted by 3-5 ml of butanol from 25 ml of 0.1 N H_2SO_4. In the butanol medium, just as in an aqueous medium, there is a linear relation between optical density and titanium concentration. In a butanol medium, 0.1 μg Ti/ml in a 10 mm cell at 490 mμ gives an extinction of 0.016.

For extracting titanium from 0.1 N H_2SO_4 at a concentration of 0.01-1 μg Ti/ml in solution, 1.5-2.0 ml of a 0.24% aqueous solution of disodium dichlorochromotropate, and 4 ml of 20% DPG chloride per 25 ml of solution should be added to the solution. At higher titanium dilutions, e.g., at titanium concentrations of the order of 0.001 μg/ml, it is not convenient to use extraction for concentrating the titanium. In such cases it is more convenient to use coprecipitation with colorless coprecipitants: this method gives good results at titanium dilutions down to $1:10^9$ (0.25 μg Ti in 250 ml). The complex of titanium with dichlorochromotropic acid is coprecipitated from 0.1 N H_2SO_4 with precipitates of diphenylguanidine α-anthracenesulfonate. The following procedure is adopted. To 250 ml of test solution which has an acidity of 0.1 N with respect to H_2SO_4, and which has a titanium concentration of 0.001 μgTi/ml or more, is added 4 ml of a 2.4% aqueous solution of disodium dichlorochromotropate and 5 ml of a 1.8% aqueous solution of potassium α-anthracenesulfonate; 6.6 ml of a 20% aqueous solution of diphenylguanidine is then added with stirring. The precipitate which settles out is filtered off through a funnel fitted with a glass filter (No. 3) or through a filter paper, and dissolved in 5 ml of butanol. The optical density of the solution obtained is measured in a 10 mm cell at 490 mμ relative to a blank prepared in parallel. The titanium content is found from a calibration curve.

Other instances of the analytical application of dichlorochromotropic acid. Preliminary experiments have shown that this reagent gives sensitive color reactions with UO_2^{2+}, Fe^{III}, and V^{IV}; and these reactions may be of interest for the photometric determination of these elements. Dichlorochromotropic acid is also of interest for the titration of zirconium, thorium, and other elements when the appropriate metalloindicators are used.

Other examples of the analytical application of dichlorochromotropic acid will be described in future communications.

The synthesis of 2,7-dichlorochromotropic acid has been described elsewhere [48].

SUMMARY

2,7-Dichlorochromotropic acid whose solutions are colorless and stable is suggested as a replacement for unstable chromotropic acid for the photometric determination of titanium. The reagent gives a raspberry color with $\mathrm{Ti^{IV}}$, a green color with $\mathrm{Fe^{III}}$, a brown color with $\mathrm{U^{VI}}$, and a yellow color with $\mathrm{Mo^{VI}}$ and $\mathrm{W^{VI}}$; Al, Zr, Mg, and Ca do not give colors with it. At pH 2.0 and at $\lambda = 490$ mμ the molar extinction coefficient is $1.12 \cdot 10^4$. Interference from $\mathrm{Fe^{III}}$ can be prevented with ascorbic acid, while interference from Mo and W can be prevented with phosphates. In order to determine titanium in solutions in which its concentration is 0.01 μg Ti/ml, its complex with dichlorochromotropic acid is extracted at pH 1 with butanol after addition of diphenylguanidine chloride. At titanium concentrations of 0.001 μg/ml, the titanium complex is first coprecipitated with a colorless organic coprecipitant, by addition of potassium α-anthracenesulfonate and diphenylguanidine chloride. The precipitate formed is filtered off, dissolved in butanol and the optical density of the solution obtained measured at 490 mμ in a 10 mm cell.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM BY MEANS OF 6,7-DIHYDROXY-2,4-DIPHENYLBENZOPYRILIUM CHLORIDE

A. I. Busev and Chang Fan
M. V. Lomonosov Moscow State University

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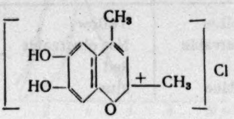
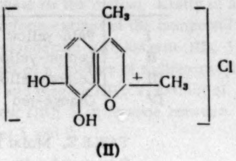
Numerous organic materials containing two hydroxy groups in the ortho position to one another in the benzene ring are reagents for sexivalent molybdenum. Examples of such reagents are pyrocatechol, pyrocatecholdisulfonic acid, stilbazo, morin, etc. It has been pointed out [1] that the two ortho arranged hydroxy groups ensure formation of characteristically colored compounds with molybdenum, and also with Ge, Sn^{IV}, Sb, and Zr. Orthodihydroxychromenols, (I-IV) which were recently suggested by Kononenko and Poluektov [2] for the photometric determination of germanium, belong to this group of potential reagents for molybdenum.



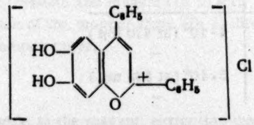
(I)

6,7-dihydroxy-2,4-dimethylbenzopyrilium chloride



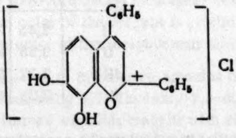
(II)

7,8-dihydroxy-2,4-dimethylbenzopyrilium chloride



(III)

6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride



(IV)

7,8-dihydroxy-2,4-diphenylbenzopyrilium chloride

They contain two ortho hydroxy groups in the benzene ring, and, as one might expect, give colored compounds with sexi- and quinquevalent molybdenum; some of them permit determination of microgram amounts of this element by an extraction-photometric method. The analytical methods which have been developed on the basis of these reagents have, in a number of instances, advantages over current methods.

EXPERIMENTAL

Solutions of the o-dihydroxychromenols* were prepared by dissolving accurately weighed aliquots of the preparations in water or ethanol (the dimethyl derivatives were dissolved in water, while the diphenyl derivatives were dissolved in ethanol). The synthesis and some of the properties of the o-dihydroxychromenols have been described in the article by Kononenko and Poluektov [2].

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* The authors would like to thank L. I. Kononenko and N. S. Poluektov who supplied us with the o-dihydroxychromenols.

Standard sodium molybdate solution was prepared by dissolving the pure salt in water; the concentration of the solution was established by means of the 8-hydroxyquinoline method [3]. One ml of solution contained on an average 4.96 mn Mo. This stock solution was diluted to give solutions of the requisite concentration.

Optical density was measured throughout on a SF-4 spectrophotometer using a cell with a path length of 1 cm. pH was measured with a pH-meter using a glass electrode.

DISCUSSION

Kononenko and Poluektov [2] have pointed out that aqueous and aqueous-ethanol solutions of the o-dihydroxychromenols, depending on the pH of the solution, have three colored forms and possess the properties of acid—base indicators.

On adding a dilute solution of sodium molybdate to solutions of o-dihydroxychromenols (I-IV) in a weakly acid medium (pH 2-3) a color change is observed (Table 1), which indicates formation of colored compounds. The latter can be extracted with chloroform and other organic solvents.

TABLE 1. Color Change of Weakly Acid Solutions of the o-Dihydroxychromenols on Adding Sodium Molybdate

Reagent	Color of aqueous solutions, pH 2-3		Color of $CHCl_3$ extracts (aqueous phase with pH 2-3)	
	reagent	molybdenum compound	reagent	molybdenum compound
I	Pale-yellow	Bright-yellow	Pale-yellow	Yellow
II	Lemon-yellow	Orange	Not observable	Not observable
III	Lemon-yellow	Red	Orange	Red
IV	Orange-red	Dirty-green	Violet-blue	Blue

TABLE 2. Molar Extinction Coefficients of Solutions of Molybdenum Compounds with o-Dihydroxychromenols

Reagent	Aqueous solution		Extract in $CHCl_3$	
	pH	E_M	pH	E_M
I	2.45	$3\cdot10^4$ (at 432 mμ)	2.2	$4\cdot10^4$ (at 470 mμ)
II	3.25	$8\cdot10^3$ (at 500 mμ)	—	—
III	2.12	$5\cdot10^4$ (at 520 mμ)	1.0	$5\cdot10^4$ (at 535 mμ)
IV	2.20	$6\cdot10^3$ (at 630 mμ)	—	—

In order to calculate the approximate values of the molar extinction coefficients, optical density measurements were made on solutions of mixtures of sodium molybdate and five times its amount of the o-dihydroxychromenols (excess of the latter cannot be reduced) at the optimum pH of the solutions and at wavelengths corresponding to the absorption maximum; the reference solution was a solution of the reagent with the same concentration and pH (Table 2). Of the four o-dihydroxychromenols studied, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride which gives an intense red colored compound with molybdate in a weakly acid medium proved to be the most sensitive reagent for molybdenum.

The colored compounds of molybdenum with the dimethyl derivatives of the chromenols are soluble in water, while those with the diphenyl derivatives are insoluble in water and precipitate out; at low concentrations of molybdate a colloidal solution is formed.

Reagents (I-IV) react analogously with a solution of a quinquevalent molybdenum salt.

The effect of pH on formation of the compound of molybdenum with the o-dihydroxychromenols was established. 2.5 ml of a 10^{-3} M solution of the reagent (I) was added to 2.5 ml of a $2\cdot10^{-4}$ M solution of sodium molybdate. The final volume was 25 ml, and the pH of the solution was adjusted by addition of hydrochloric acid or sodium hydroxide, establishment of the requisite pH being controlled by means of a glass electrode. The optical density was measured at 440 mμ relative to water. The results obtained are given in Fig. 1 (curve 1). Experiments were carried out in the same way with solutions of the reagent (I) of equal concentration (Fig. 1, curve 2). The difference curve (Fig. 1, curve 3) shows the relationship between formation of the molybdenum compound and the pH of the solution. The optimum value of the acidity of the solution for color development is found within the narrow pH range 2.5-3. Over this same interval there is a sharp increase in the optical density of a solution of the reagent itself. All this complicates the use of reagent (I) for the photometric determination of molybdenum in aqueous solutions. Similar results were obtained in aqueous solutions with the other o-dihydroxychromenols. In the case of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride the optimum pH of the solutions is 2.

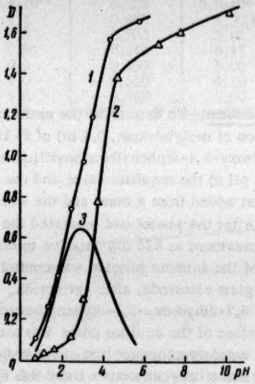


Fig. 1. Effect of pH on the optical density of solutions of the compound of molybdenum with reagent (I). 1) Solution of a mixture of sodium molybdate and reagent (I); 2) solution of the reagent alone (I); 3) difference curve.

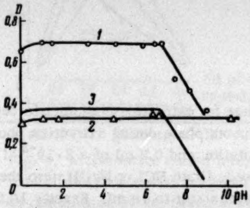


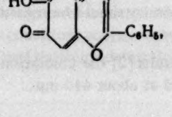
Fig. 2. Effect of the pH of the aqueous phase on the optical density of a chloroform extract of the compound of molybdenum with reagent (III). 1) Extract of a mixture of sodium molybdate and reagent (III); 2) extract of reagent (III); 3) difference between curves 1 and 2.

Determination of molybdenum by means of the o-dihydroxychromenols by measuring the optical density of aqueous solutions is not expedient, since it is necessary to take at least a four-fold excess of reagent over the molybdenum, and the color of the reagent is partially superimposed on the color of the molybdenum compound formed.

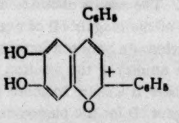
Determination of microgram amounts of molybdenum is best carried out using 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride as the reagent, extracting the molybdenum compound formed with this reagent with chloroform, and measuring the optical density of the extract. This variant of the method possesses a high sensitivity, is readily carried out, and gives completely satisfactory results.

6,7-Dihydroxy-2,4-dimethylbenzopyrilium chloride is less suitable for the extraction photometric determination of molybdenum since the optical density of the chloroform extract in this case is strongly dependent on the pH of the aqueous phase.

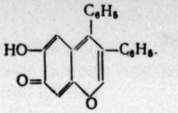
It is interesting to note that a chloroform extract of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride has an orange color, and the optical density of the extract at 535 mμ is independent of the pH of the aqueous phase (Fig. 2, curve 2). It is probable that in this case only undissociated molecules of the orange colored anhydro base are extracted:



during extraction the reagent changes from the ionic form



into the molecular form



pH Range for extraction photometric determination of molybdenum. To determine the optimum value of the pH of the aqueous phase during extraction photometric determination of molybdenum, 0.4 ml of $2\cdot10^{-4}$ M sodium molybdate solution and 0.2 ml of a $2\cdot10^{-3}$ M solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride in alcohol were mixed; dilute HCl or NaOH were then added to adjust the pH to the requisite value and the mixture obtained was diluted with water to 10 ml. Exactly 10.0 ml of $CHCl_3$ was next added from a buret and the whole vigorously shaken for 4 min. After the phases had separated the optical density of the extract was measured at 535 mμ relative to chloroform (Fig. 2, curve 1). The pH of the aqueous solution was controlled by means of a pH-meter with a glass electrode, after extraction. The optical density of an extract of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride at various pH values of the aqueous phase was measured in the same way, but at a constant concentration of the reagent (Fig. 2, curve 2). The difference between curves 1 and 2 is shown by curve 3. It is clear that the optical density of the extract of the molybdenum compound is independent of pH over a large pH range of the solution (1-6.5).

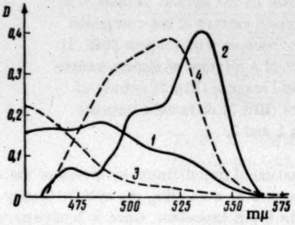


Fig. 3. Absorption curves. 1) $CHCl_3$ extract of reagent (III); 2) extract of the compound of molybdate with reagent (III) (in $CHCl_3$); 3) 50% aqueous-acetone solution of reagent (III); 4) 50% aqueous-acetone solution of the compound of molybdate with reagent (III).

At pH < 1 low results were obtained because of incomplete extraction of molybdenum. At pH higher than 6.5 a sharp decrease in optical density was observed, although, according to published results, it is the molybdate anion MoO_4^{2-} which is mainly present in solution. Probably, the reagent forms a stable compound with the molybdenyl cation MoO_2^{2+}.

The optical properties of solutions of the molybdenum compound. The absorption curve of a $8\cdot10^{-6}$ M solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride in a 1:1 mixture of water and acetone at pH 2.12 relative to water is shown in Fig. 3 (curve 3). The absorption maximum is located at 450 mμ; * addition of molybdate to the reagent leads to a shift in the maximum toward the higher wavelengths. The absorption curve of the compound of molybdenum with the reagent in 50% acetone has a maximum at 520 mμ (Fig. 3, curve 4). The sodium molybdate and reagent concentrations in this case were $4\cdot10^{-5}$ and $8\cdot10^{-6}$ M respectively at pH 2.12. The optical density was measured relative to a solution of the reagent with the same concentration. The absorption curve of a chloroform extract of the molybdenum compound has a maximum at 535 mμ (Fig. 3, curve 2). The extract was obtained by the same method as that used in establishing the optimum pH value of the aqueous solution during extraction. The optical density was measured relative to a chloroform extract of the reagent. The chloroform extract has an orange color. There is a diffuse maximum at 485 mμ on the absorption curve of a $8\cdot10^{-6}$ M solution of the reagent. An extract of the reagent itself also absorbs light at 535 mμ. Accordingly, during photometric determination of molybdenum, the optical density should be measured relative to an extract of the reagent of the same concentration.

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* According to Kononenko and Poluektov's results [2] the absorption maximum of aqueous solutions of the reagent containing 1.0% ethanol and gelatin, is found at about 440 mμ.

The molar extinction coefficient of a chloroform extract of the complex was determined at 535 mμ in the presence of excess of reagent (III) ($1.0 \cdot 10^{-4}$ M) in the aqueous phase. The mean value of seven measurements is $(5.04 \pm 0.03) \cdot 10^4$ (Table 3).

TABLE 3. Molar Extinction Coefficients of Extracts of the Compound of Molybdenum with Reagent (III)

C_{Mo}, M	$D_l^{535} = 1$ cm	E_M^{535}
$0{,}4 \cdot 10^{-5}$	0,202	$5{,}0 \cdot 10^4$
1,2	0,585	4,90
1,8	0,903	5,02
0,8	0,410	5,13
0,5	0,250	5,00
1,0	0,520	5,20
1,5	0,750	5,00
	Mean	$(5{,}04 \pm 0{,}03) \cdot 10^4$

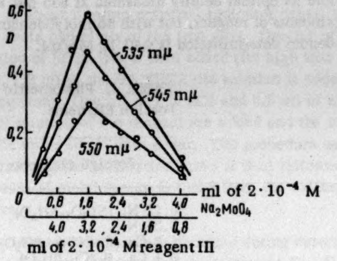


Fig. 4. Molar ratios during interaction of molybdate with reagent (III) as determined by the isomolar series method. The chloroform extract was diluted to 25.0 ml. The optical density was measured relative to chloroform. A correction was applied for the absorption of the reagent.

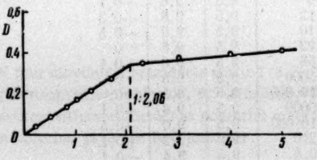
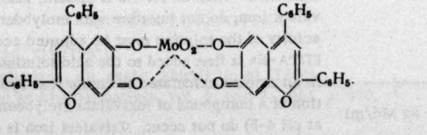


Fig. 5. Molar ratio during interaction of molybdate with reagent (III) as determined by the method of varying the concentration of one of the components. The molar ratio of Mo^{VI} to reagent (III) is plotted along the abscissa.

The composition of the complex. The molar ratio which holds during interaction of molybdenyl ions and 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride was established by the isomolar series method (Fig. 4) and by the method of varying concentrations of one of the components (Fig. 5). The maximum absorption is found at a molar ratio of molybdate to reagent of 1 : 2 (Fig. 4). In the method in which the concentration of one of the components was varied, during the preparation of series of extracts, the final concentration of sodium molybdate in the aqueous phase was kept constant at $8 \cdot 10^{-6}$ M, while the reagent concentration was varied from $1.6 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ M. The optical density was measured at 535 mμ relative to an extract of the reagent of the same concentration under the same conditions. A sharp break on the straight line was observed at a molar ratio of molybdate to reagent of 1 : 2.6 (Fig. 5).

Thus in an acid medium, reagent (III) forms a stable compound, apparently, with the molybdenyl cation:



Determination of molybdenum. 6,7-Dihydroxy-2,4-diphenylbenzopyrilium chloride enabled us to develop an extraction photometric method for determining small amounts of molybdenum in the presence of a series of elements.

It follows from Fig. 5 that during determination of microgram amounts of molybdenum there is no need to add a large excess of reagent. Special experiments showed that it is sufficient to shake for 2-5 min in a 0.1 M HCl medium. The optical density of extracts does not change over a period of several days. The optimum acidity of the aqueous phase is about 0.1 M HCl. Under these conditions sodium ethylenediaminetetracetate (EDTA-Na) masks Fe^{3+} and other ions, and does not interfere with molybdenum determination.

A calibration curve is constructed by introducing 8.5 ml of an almost neutral standard solution of sodium molybdate containing not more than 20 μg molybdenum into a separating funnel; 1 ml of 1 M HCl is then added, followed by exactly 0.5 ml of a $2 \cdot 10^{-3}$ M ethanolic solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride measured out with a pipet. Exactly 10.0 ml of chloroform measured out of a buret is added to the mixture obtained, and the contents of the funnel are vigorously shaken for 3-5 min. After the phases have separated out the orange colored organic phase is isolated (if a turbidity should appear the phase is allowed to stand for the solution to become clear) and its optical density measured at 535 mμ relative to an extract prepared under the same conditions using the same amounts of reagent, but with no molybdenum. Extracts conform to Beer's law (Fig. 6). The sensitivity for molybdenum determination is 0.01 μg Mo/ml.

TABLE 4. Photometric Determination of Molybdenum in the Presence of Foreign Elements

Foreign elements (Me), mg	Ratio Mo: Me	Mo, μg		
		taken	found	error
0,12 Ni ($NiSO_4 \cdot 5H_2O$)	1 : 12	9,5	9,5	0
0,24 Ni	1 : 24	9,5	9,7	+0,2
1,2 Co ($Co(NO_3)_2 \cdot 6H_2O$)	1 : 120	9,5	9,5	0
0,4 Ca ($CaCl_2 \cdot 6H_2O$)	1 : 40	9,5	9,5	0
1,3 Zn ($Zn(NO_3)_2 \cdot 4H_2O$)	1 : 130	9,5	9,6	+0,1
0,06 Cu ($CuSO_4 \cdot 5H_2O$)	1 : 6	9,5	9,6	+0,1
0,12 Cu	1 : 12	9,5	9,8	+0,3
0,1 Cr ($Cr(NO_3)_3 \cdot 6H_2O$)	1 : 10	9,5	9,0	−0,5
0,21 Cr »	1 : 22	9,5	9,5	0
0,55 Mn ($MnCl_2 \cdot 4H_2O$)	1 : 58	9,5	9,6	+0,1
50 50 EDTA-Na	1 : 5000	9,5	9,5	0
100 »	1 : 10 000	9,5	9,5	0
50 Tartaric acid	1 : 5000	9,5	9,6	+0,1
100 » »	1 : 10 000	9,5	9,0	−0,5
2,1 Bi ($Bi(NO_3)_3 \cdot 5H_2O$)*	1 : 210	19,0	19,2	+0,2
0,04 Ti ($TiO(SO_4)_2$)*	1 : 0,4	9,5	9,4	−0,1
0,04 Ti ($TiO(SO_4)_2$)*	1 : 2,1	19,0	19,2	+0,2
0,07 Ti ($TiO(SO_4)_2$)*	1 : 7	9,5	12,6	+3,1
1,1 Fe ($FeCl_3 \cdot 6H_2O$)*	1 : 58	19,0	19,0	0
5,6 Fe ($FeCl_3 \cdot 6H_2O$)*	1 : 560	9,5	9,6	+0,1
33,6 Fe ($FeCl_3 \cdot 6H_2O$)**	1 : 3530	9,5	9,1	−0,4

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* In the presence of 1 ml of 5% EDTA-Na solution.

** 1.2 ml of 5% EDTA-Na solution was added per 10 mg Fe.

Molybdenum was determined in synthetic mixtures using the same conditions as those employed for constructing a calibration curve, except that before adding hydrochloric acid, the pH of the solution was adjusted to about 2 using universal indicator paper. The results obtained are given in Table 4. Nickel, cobalt, calcium, zinc, copper, divalent manganese, trivalent chromium, EDTA-Na, and tartaric acid do not interfere with molybdenum determination. When EDTA-Na is present, bismuth and even large amounts of trivalent iron, do not interfere with molybdenum determination either. The acidity of the solution must be adjusted accurately in the presence of iron; EDTA-Na is first added to the acid solution (pH about 2), HCl is then added in an amount calculated to ensure that hydrolysis of the iron salt and formation of a compound of sexivalent molybdenum with EDTA-Na (which is formed at pH 4-5) do not occur. Trivalent iron is completely masked by EDTA-Na at pH 1 and does not interfere with determination; under these conditions a precipitate of ethylenediaminetetracetic acid may settle out (particularly in the presence of large amounts of EDTA-Na), but this does not interfere with the determination. Tungsten interferes with molybdenum determination.

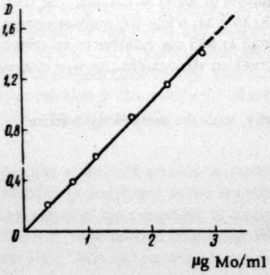


Fig. 6. Calibration curve.

Determination of molybdenum in steel is carried out as follows. An aliquot of steel (about 0.1 g) is dissolved in a mixture of 5 ml HNO_3 (1 : 1) and 5 ml H_2SO_4 (1 : 1) contained in a 100 ml beaker, and the solution evaporated to the appearance of white fumes of H_2SO_4. If the steel should not dissolve completely, a few ml of HCl (1 : 1) is

added and the liquid evaporated to dryness; this operation is repeated several times until solution is complete. After cooling, 20 ml of water is added and the liquid heated until the salts have dissolved. The insoluble silica is filtered off through a filter paper, the filter paper plus insoluble residue is washed several times with the minimum amount of water, and the filtrate collected in a 50 ml standard flask. After cooling, the filtrate is diluted to the mark with water, a suitable aliquot of this solution is pipetted into a separating funnel, water is added and the pH carefully adjusted to about 2 (using universal indicator paper) in order to avoid hydrolysis of the iron salts. One ml of a 5% solution of EDTA-Na is then added (for high iron contents, 1.2 ml of the 5% EDTA-Na solution is added per 10 mg iron). One ml of 1 N HCl and 0.5 ml of a $2\cdot10^{-3}$ N solution of the reagent are added and the solution made up to 10 ml with water. The procedure used for constructing the calibration curve is then followed. The amount of molybdenum is found from the calibration curve.

TABLE 5. Determination of the Molybdenum Content of Standard Steel Sample No. 31 b. (0.27% Mo). 0.44% C, 0.365% Mn, 0.275% Si, 0.017% S, 0.023% P, 1.24% Cr, 3.40% Ni

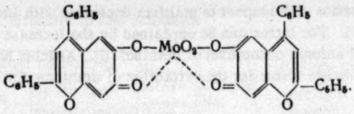
Sample	Mo found, %	Error
1	0.25	−0.02
	0.26	−0.01
2	0.27	0
	0.26	−0.01
3	0.27	0

Satisfactory results were obtained during determination of molybdenum in standard steel, sample No. 31 b (Table 5).

SUMMARY

Of four dihydroxychromenols studied (6,7-dihydroxy-2,4-dimethylbenzopyrilium chloride, 7,8-dihydroxy-2,4-dimethylbenzopyrilium chloride, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride, and 7,8-dihydroxy-2,4-diphenylbenzopyrilium chloride) as potential reagents for sexivalent molybdenum, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride gave the best results.

The composition of the compound formed between molybdenum and 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride has been established:



The molar extinction coefficient is $5.04 \pm 0.03\cdot10^4$.

An extraction photometric method has been developed for the determination of molybdenum in steels. The sensitivity of the method is 0.01 μg Mo/ml. The method permits determination of microgram amounts of molybdenum in the presence of nickel, cobalt, calcium, zinc, copper, manganese, and chromium. Bismuth and large amounts of iron do not interfere when sodium ethylenediaminetetracetate is present. Tungsten interferes.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION 4.* PHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF ARSENAZO I AFTER SEPARATION OF URANIUM FROM IMPURITIES BY MEANS OF THE ANION EXCHANGE RESIN ÉDÉ-10P

L. M. Moiseeva, N. M. Kuznetsova, V. F. Luk'yanov,
and G. L. Sel'manova

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A fairly large amount of work has been devoted to studying the sorption of uranium with anion exchange resins from various media. Some of the results obtained have already found practical application. The most interesting methods are those based on extraction of uranium from sulfuric acid media with strongly basic anion exchange resins. In sulfuric acid solutions, uranium, in practice, forms only one complex with the ratio $UO_2^{2+} : SO_4^{2-} = 1:1$, which is not charged [1-2]. Nevertheless, uranium is readily sorbed by anion exchange resins; this is only possible under conditions in which it is found in solution in the form of an anion. According to Arden, Wood [3] and Miller [4] a negatively charged uranium complex is formed during sorption on the resin surface. One or two SO_4^{2-} ions from the resin add on to the UO_2SO_4 complex and give it a negative charge. The sorption mechanism can be expressed by the following equation:

$$2R_2SO_4 + UO_2SO_4 = R_4[UO_2(SO_4)_3].$$

The capacity of anion exchange resins with respect to uranium decreases with increasing SO_4^{2-} ion concentration and with the acidity of the solution [5]. The latter can be explained by the increase in HSO_4^- ions in solution and on the resin, which prevents formation of anionic complexes of uranium [6]. Articles have been published on the use of the following strongly basic anion exchange resins for the extraction of uranium: Amberlite IRA 400 [7], Dowex 1 [8], and Dowex 2 [9].

The aim of the work described here was to study the application of the Russian anion exchange resin ÉDÉ -10P for extracting uranium from ores and processed products of these ores, with subsequent determination of uranium by means of Arsenazo I. The work reduced to establishing the optimum conditions for selective sorption of uranium from sulfuric acid solutions and for its complete desorption from the resin.

Five-seven ml of resin with a particle size of 0.2-0.4 mm was introduced into a column 10 mm in diameter and was washed with 10% hydrochloric acid until the eluate gave a negative reaction for trivalent iron with potassium thiocyanate. The resin was then converted into the SO_4 form by washing it with 5% ammonium sulfate with a pH of 1-1.5 until the pH of the liquid issuing from the column was equal to the pH of the solution passed into it. One M $HClO_4$ was used initially for eluting uranium.

Uranium is sorbed quantitatively at pH 0.5-3.5 on passing a solution through the column at the maximum possible rate of 4-5 ml/min. Uranium is eluted completely with 100 ml of perchloric acid solution passed through the column at the rate of 2-2.5 ml/min.

Since perchloric acid is not always available, an attempt was made to replace it by a mixture of nitric acid and ammonium nitrate. Uranium elution curves obtained on using such mixtures, with varying composition, are shown in Figs. 1 and 2. It is clear that the eluting action of the mixture is determined, in the main, by the nitrate ion concentration. The optimum nitrate ion concentration appears to be 1 M. Experiments showed that the most effective mixture is one which is 3% with respect to ammonium nitrate and 5% with respect to nitric acid. One-hundred ml of such a solution passed through the column at the rate of 2.0-2.5 ml/min is sufficient for eluting 2 mg uranium.

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* For communication 3 see [10].

The effect of various cations and anions on the sorption of uranium and its subsequent photometric determination with arsenazo I has been studied. It was found that sexivalent molybdenum, although it is sorbed with the uranium, does not interfere with its subsequent determination with arsenazo I, and can therefore be present in appreciable amounts. In the presence of quinquevalent vanadium which interferes with the determination of uranium with arsenazo I, sorption of the uranium should be carried out at pH values ≤ 1, or a reducing agent should be added to the solution. We used a saturated solution of hydrazine sulfate as a reducing agent; when this is done sorption of vanadium only starts at pH ≥ 2.7.

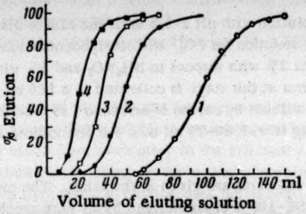

Fig. 1. Elution curves of uranium from the resin ÉDÉ-10P with 3% ammonium nitrate solution, as a function of the HNO_3 content of the solution. The figures on the curves relate respectively to: 1) 1; 2) 3; 3) 5; 4) 10 ml of concentrated HNO_3 in 100 ml of solution.

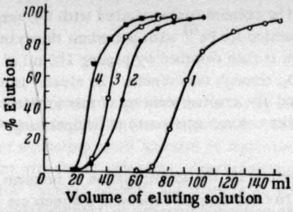

Fig. 2. Elution curves of uranium from the resin ÉDÉ-10P with 3% nitric acid solution, as a function of the NH_4NO_3 content of the solution. The figures on the curves relate respectively to: 1) 1; 2) 3; 3) 5; 4) 10 g of NH_4NO_3 in 100 ml of solution.

Determination of Uranium in Ore Standards

Sample No.	Uranium content, %		No. of determinations	Sample No.	Uranium content, %		No. of determinations
	specified content	by the suggested method			specified content	by the suggested method	
1	0,103±0,002	0,102±0,002	24	6	2,48 ±0,04	2,47 ±0,01	10
2	0,220±0,010	0,217±0,004	9	7	0,059 ±0,004	0,058 ±0,001	14
3	0,530±0,009	0,538±0,004	16	8	0,070 ±0,001	0,070 ±0,001	8
4	0,092±0,008	0,093±0,003	10	9	0,563 ±0,011	0,561 ±0,009	10
5	0,220±0,010	0,211±0,001	8	10	0,0725±0,0004	0,0710±0,001	14

Phosphate ions interfere with the photometric determination of uranium; they are not held firmly by the resin, however, and can be readily removed from the column by eluting the latter with 150-200 ml of ammonium sulfate with pH 0.5-1. When samples contain large amounts of phosphorus, uranium is sorbed at pH 0.5, otherwise a precipitate of uranium forms on establishing the medium. A pH of about 0.5 is also necessary during sorption of uranium from solutions containing titanium. At higher pH values Ti hydrolyzes in the column and interferes with subsequent determination of uranium.

Interference from Cl^- and excess SO_4^{2-} on sorption of uranium was not detected even a molar ratios of 1:15,000 and 1:400,000 respectively. Iron and copper are quantitatively separated from uranium on eluting the column with 150-200 ml of 5% ammonium sulfate solution. Completeness of separation from these elements was checked by testing the eluate for Fe^{III} potassium thiocyanate.

On the basis of the work carried out the following method is suggested for determination of uranium in ores.

EXPERIMENTAL

A 0.5 g aliquot of ore (for uranium contents of 0.01-0.1%) is decomposed with hydrochloric acid and hydrogen peroxide. As soon as only 2-3 ml of liquid remains in the flask it is cooled, 5-7 ml of concentrated sulfuric acid is added and the liquid evaporated to a volume of 1-2 ml. Evaporation to dryness is not recommended since in such cases low results are obtained, particularly in the presence of phosphorus. Twenty-twenty-five ml of water is added and the liquid boiled for 5-7 min under a watch glass; the insoluble residue is filtered off and the filtrate diluted to 70-80 ml.

When the sample contains vanadium, 2-5 ml of a saturated hydrazine sulfate solution is added to the filtrate obtained and the pH adjusted to 1.0-1.5 by means of ammonia. When a sample contains a large amount of phosphorus and titanium, the pH of the solution should be adjusted to 0.5.

The requisite pH value is established using methyl violet as external indicator (first color change from yellow to green at pH 0.5; second color change from green to blue at pH 1.0-1.5).

The original solution prepared in this way is passed through a column at the rate of 4-5 ml/min.

The column is next washed with 5% ammonium sulfate solution with pH 1-1.5 until the eluate gives a negative reaction for Fe^{III} with potassium thiocyanate, or a negative reaction for PO_4^{3-} with molybdenum solution; the uranium is then desorbed by passing 100 ml of a solution which is 3% with respect to NH_4NO_3 and 5% with respect to HNO_3, through the column. The eluate issuing from the column at this stage is collected in a 100 ml standard flask and the uranium content of this solution determined on an aliquot by means of arsenazo I as described earlier [10]. The column is restored to its operating condition by eluting it with 50-70 ml of a 5% ammonium sulfate solution.

Results for the determination of uranium in a series of ore standards are given in the table. The method is very simple to carry out; no expensive reagents are required. Resin ÉDÉ-10P is characterized by its high mechanical stability and by its resistance to various types of chemical action; we were able to work with one lot of resin for 18 months. Ten to fifteen determinations can be carried out in 10 hr.

SUMMARY

A method has been developed for the photometric determination of uranium in ores by means of arsenazo I after preliminary removal of uranium from impurities with the anion exchange resin ÉDÉ-10P.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

SEPARATION OF RHENIUM AND MOLYBDENUM BY COPRECIPITATION OF THE LATTER WITH FERRIC HYDROXIDE

A. I. Novikov

V. I. Lenin Tajik State University, Stalinabad

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Rhenium and molybdenum are separated most often by extraction, by chromatographic methods, by precipitation of certain sparingly soluble compounds, and by distillation of rhenium on heating the solution [1]. These methods differ very much from each other in the efficiency of separation. For separating small amounts of septivalent rhenium and sexivalent molybdenum we have used coprecipitation of the latter with ferric hydroxide. Coprecipitation of perrhenate ions with ferric hydroxide does not exceed a few percent at low rhenium contents and when large amounts of carrier are used [2]. These results were confirmed again under the conditions used for separating rhenium and molybdenum.

First of all we studied the behavior of rhenium and molybdenum, taken separately, during precipitation of ferric hydroxide, and then precipitated the carrier in the presence of perrhenate and molybdate ions. The amount of rhenium remaining in solution and entrained by the precipitate was controlled by means of the radioactive isotope Re^{186}, whose activity was measured with a special quartz cell on a B-2 setup described earlier [3]. In some instances rhenium was determined photometrically by the thiocyanate method. The amount of molybdenum in solution and in the precipitate was determined by the thiocyanate method on a FÉK-N-57 microphotocolorimeter fitted with a No. 3 filter (maximum transmission at 453 mμ). A No. 2 filter with maximum transmission at 413 mμ (Fig. 1) can be used for rhenium determination.

Molybdenum was determined by the same method in all experiments [4]. About 7 ml of an acid mixture (725 ml water, 225 ml H_2SO_4, and 50 ml HCl), 3 ml of a 25% solution of potassium thiocyanate, and 0.5 ml of 10% $SnCl_2 \cdot 2H_2O$ or water were added to the molybdenum containing solution and the volume made up to 25 ml. After mixing, the solution was poured into a cell and its optical density measured; the latter was always measured after the same time interval after addition of the $SnCl_2 \cdot 2H_2O$, since the color intensity changes slightly (curves 4 and 5 in Fig. 1) with time. Special experiments showed that the optical density of solutions of the thiocyanate compound of molybdenum decreases more rapidly the greater the amount of $SnCl_2$.

Coprecipitation was studied under the following conditions: volume of solution 20.0 ml; amount of carrier 0.2 mg at of iron (10.2 mg Fe); NH_4Cl concentration, 1 M; temperature 17°; contact time of solution with precipitate 10-30 min. Ferric hydroxide was precipitated by addition of alkali (potassium hydroxide, ammonia, pyridine) to an acid solution containing iron chloride, molybdate, and perrhenate. The precipitate was separated from the solution by centrifuging. After removal of the precipitate, all the solution was placed in the cell in which the radioactivity of rhenium was measured; subsequently, using a LP-5 pH-meter the pH of the solution was determined. The precipitate was dissolved in 2 ml of 2 N hydrochloric acid; this solution was poured into a beaker containing 10 ml of 0.8 N potassium hydroxide. After centrifuging, the solution was diluted to 20 ml and the molybdenum determined on an aliquot by the thiocyanate method. Under these conditions no coprecipitation of molybdenum with ferric hydroxide was observed.

The amount of solution lost in impregnating the precipitate and remaining on the beaker walls and the centrifuge tubes amounts to about 3-4% of the original volume of solution (20 ml) in the case of 10 mg of iron.

During a study of the coprecipitation of small amounts of rhenium (from 0.2 to 100 μg) it was found that under the experimental conditions used (pH from 5 to 10; NH_4Cl concentration, 1 N) no coprecipitation of rhenium with ferric hydroxide is observed, i.e., the extent of coprecipitation for the most part is zero, and does not exceed 2-3%

of the original amount of rhenium in individual cases, this being approximately equal to the experimental error. Coprecipitation of 1 mg of molybdenum with ferric hydroxide amounts over a certain pH range to 100% and decreased to zero on increasing the pH further (Fig. 2). During precipitation of the carrier in the presence of molybdenum and rhenium, the ratio between rhenium and molybdenum was varied from 1:10 (1 mg Mo: 100 μg Re) to 1:5,000 (1 mg Mo: 2 μg Re). Determination of rhenium and molybdenum in the precipitate of the carrier by Sandell's method [5], which consists in separating Mo and Re by ether extraction of hydrochloric acid solutions of the thiocyanate complex of molybdenum in the presence of mercury, and photometric determination of Re and Mo, showed that that up to 15% of the rhenium taken was present in solution, while the use of the radioactive isotope Re^{186} indicated that the precipitate only contained 2-3% of the rhenium, the latter coming from the solution impregnating the precipitate. Apparently, the extraction method described is not good enough to ensure complete extraction of molybdenum, and therefore leads to errors in rhenium determination.

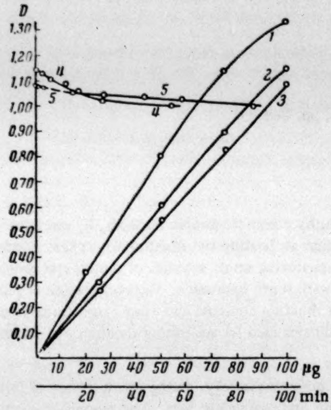

Fig. 1. Calibration curves for rhenium and molybdenum. Change in optical density of solution with time. 1) Re, filter No. 2; 2) Re, filter No. 3; 3) Mo, filter No. 3; 4) and 5) time plotted along the abscissa, Re (4) and Mo (5) in solution.

Results of the study of separating molybdenum and rhenium are given in the table.

During coprecipitation of 1 mg of molybdenum with 0.1 mg atom of iron, incomplete entrainment of the molybdenum by the precipitate occurs (about 94%) at pH 4-5. Presumably, molybdenum enters into the composition of the precipitate in the form of dimeric or polymeric ions, since precipitation is carried out from weakly acid solution. If it is assumed that the precipitate contains ferric hydroxide and normal ferric molybdate, then the composition of the precipitate can be written as $15Fe(OH)_3 \cdot Fe_2(MoO_4)_3$. It can be assumed therefore that the solid phase consists mainly of the carrier — ferric hydroxide — with which the molybdenum is coprecipitated. Complete coprecipitation of 1 mg of molybdenum with ferric hydroxide occurs when the amount of carrier used is greater than 0.1 mg at; 0.2 mg at. of iron is quite sufficient for this purpose. On the basis of the results given in Fig. 2 and in the table, one can make the following conclusions regarding the separation of molybdenum and rhenium by coprecipitation of molybdenum with ferric hydroxide: perrhenate ions, even at low concentrations (from $5 \cdot 10^{-8}$ to $2.7 \cdot 10^{-5}$ g. ion/liter) are hardly coprecipitated at all with ferric hydroxide; 1 mg of molybdenum is completely coprecipitated with 0.2 mg at of iron precipitated as its hydroxide at pH values for incipient coagulation up to 7.5 [7]; on increasing the pH further to 10.5 coprecipitation of molybdenum drops to 0; changes in ammonium chloride concentration from 0.2 to 2 M have no effect on coprecipitation of molybdenum with ferric hydroxide; variations in the contact time of precipitate with solution from 1-2 m to 30 min do not affect the extent to which molybenum is coprecipitated with the carrier.

Separation of Mo and Re by Coprecipitation of Mo with Ferric Hydroxide

Expt. No.	pH	NH_4Cl concentration M	Rhenium				Molybdenum					
			taken		found in solution		Loss, %	Coprecipitated, %	taken	found in the precipitate		Coprecipitated, %
			μg	cpm	cpm	μg			μg	D	μg	
1	4,98	1	10	3100±16	3026±16	9,76	3	0	1000	1,09	1020	102
2*	5,48	1	10	3040±16	2972±16	9,72	3	0	1000	1,07	1000	100
3	6,12	1	10	3050±16	2930±16	9,61	3	1	1000	1,07	1000	100
4	9,10	1	10	2643±14	2510±14	9,58	3	1,2	1000	0,385	350	35
5*	5,52	2	10	1390±10	1332±10	9,58	3	1,2	1000	1,06	990	99
6*	5,30	0,2	10	1423±12	1390±12	9,70	3	0	1000	1,06	990	99
7*	5,51	1	0,2	461±3	416±5	0,187	3	3,5	1000	1,08	1020	102
8	8,30	1	0,2	455±5	422±5	0,136	3	4	1000	0,75	685	68,5
9												

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* In these experiments ferric hydroxide was precipitated by dropwise addition of 0.08 ml of pyridine until coagulation of the precipitate.

Accordingly, the following technique can be recommended for separating and determining small amounts of rhenium and molybdenum: to a hydrochloric acid solution containing rhenium and molybdenum in the highest oxidized form is added ferric chloride at the rate of about 10 mg iron per mg molybdenum; this is followed by ammonium chloride, and then pyridine or ammonia dropwise until the NH_4Cl concentration lies within the limits 0.2-2 M and until the ferric hydroxide is precipitated and coagulated, but not enough to bring the pH above 7. The precipitate which contains all the molybdenum is separated from the solution in which the rhenium is determined by the thiocyanate method. The precipitate is dissolved in hydrochloric acid and this solution is poured into excess alkali; during this stage all the molybdenum dissolves. After removal of the hydroxide by centrifuging, molybdenum is determined in the solution.

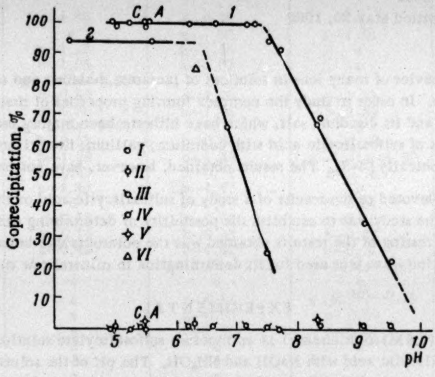

Fig. 2. Coprecipitation of molybdenum and rhenium with ferric hydroxide. 1) Coprecipitation of Mo (0.2 mg at. Fe); 2) ditto (0.2 mg at. Fe; I) Mo = 1 mg; II) Re = 1 μg; III) Re = 10 μg; IV) Re = 100 μg; V) Re = 0.2 μg; VI) Mo = 2 mg; Fe = 0.2 mg at. Points A and C, precipitation with pyridine.

The method suggested is very simple and is applicable to a wide range of molybdenum to rhenium ratios; their separation is complete. The whole operation can be carried out in 10-15 min.

A similar separation method can, as special experiments showed, be applied to the separation of tungsten and rhenium.

SUMMARY

Perrhenate ions are hardly coprecipitated at all with ferric hydroxide under varying conditions. Coprecipitation of molybdenum with ferric hydroxide amounts to 100% over a certain pH range, but can drop to 0.

A simple and rapid method based on coprecipitation of molybdenum with ferric hydroxide at pH < 7.5 is suggested for separating molybdenum and rhenium.

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THE USE OF HYDROXY ACIDS IN POLAROGRAPHIC ANALYSIS

COMMUNICATION 2. DETERMINATION OF MANGANESE IN A SULFOSALICYLATE MEDIUM*

I. Adam, J. Dolezal, and J. Zyka

Charles University, Prague (Czechoslovakia)

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The polarographic behavior of many ions in solutions of lactates, malates, and salicylates [1] was the subject of an earlier communication. In order to study the complex forming properties of materials of the given type further, we chose sulfosalicylic acid and its disodium salt, which have hitherto been mainly used during photometric determinations [2, 3]. Complexes of sulfosalicylic acid with cadmium, gallium, iron, titanium, nickel, and manganese have been studied polarographically [4-7]. The results obtained, however, have not been used for analytical purposes.

The present article is devoted to the results of a study of sulfosalicylic acid or its disodium salt as supporting electrolytes; the purpose of the study was to establish the possibility of determining certain ions, in particular, in a alkali media. The most interesting of the restults obtained was the polarographic behavior of the complex of divalent manganese, whose reduction wave was used for its determination in mineral raw material.

EXPERIMENTAL

Sodium sulfosalicylate (0.4 M) solution and 1 M ammonium sulfosalicylate solution were prepared by mixing equivalent amounts of sulfosalicylic acid with NaOH and NH_4OH. The pH of the solutions of the sulfosalicylates was adjusted to a value dependent on the buffer used (Clark and Lebs or borate buffer) by addition of sodium hydroxide or ammonia until the requisite value was obtained, after addition of the salts of test elements.

Polarographic curves were recorded on a V. 301 Heyrovsky polarograph with a 30 galvanometer, using a Calousek cell fitted with a saturated calomel electrode.

Results. Results of the polarographic behavior of individual ions are given in the table. On the basis of preliminary experiments it was established that, from a practical point of view, the most interesting feature is the polarographic behavior of manganese. Divalent manganese in a medium of 0.4 M sodium sulfosalicylate at pH 8-9 gives a colorless complex, as a result of the depolarization of which there appears a wave with a diffusion character at negative potentials (at approximately −0.80 v). On increasing the alkalinity of the solution by addition of sodium hydroxide, gradual oxidation of the divalent manganese complex by atmospheric oxygen to a trivalent manganese complex commences and the solution acquires an olive-brown color. The oxidation rate (followed polarographically) increases on increasing the pH and reaches a maximum at a concentration of 0.1 M NaOH and 0.4 M sodium sulfosalicylate. At higher alkali concentrations precipitation of manganese commences, probably as its hydroxide.

Oxidation of the divalent manganese complex by atmospheric oxygen is manifested polarographically by the appearance of a developed reduction wave with a very positive potential in the range + 0.02 v to −0.17 v (saturated calomel electrode). With increasing alkalinity of the solution the half-wave potential shifts to more negative values.

On increasing the sodium sulfosalicylate concentration, while keeping the sodium hydroxide concentration constant ($5 \cdot 10^{-2}$ M), the half-wave potential hardly changes at all, while the wave height increases. At sodium sulfosalicylate concentrations less than $5 \cdot 10^{-2}$ M (NaOH concentration = $5 \cdot 10^{-2}$ M) a precipitate is formed. It follows therefore that the most suitable electrolyte is a solution of $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. In this medium the half-wave potential of the trivalent manganese complex is equal to −0.14 v (saturated calomel electrode). The diffusion character of the wave is confirmed by the linear relationship between the value of the diffusion current and the height of the mercury reservoir, and also between the value of the diffusion current and the manganese concentration over the range $1\cdot10^{-3} - 1\cdot10^{-4}$ M. In this medium quantitative oxidation of divalent manganese is complete within only 3 min as a result of the action of air on the solution. The wave height does not change further even under the continued effect of air; it does not matter therefore how long the solution remains in air after it has been oxidized. No maximum appears on the curve.

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* Communication 1, see [1].

Half-wave Potentials of Certain Ions in Sodium and Ammonium Sulfosalicylate

Ion			Media	
	sodium sulfosalicylate		ammonium sulfosalicylate	
	pH 6	pH 8	pH 13	pH 14
Fe^{2+}	a—1,36	a—0,70	e	e
Fe^{3+}	e	a—1,02	a—1,08	a—0,69
Co^{2+}	a—1,32	b—1,46	e	a—1,34
Ni^{2+}	b—1,04	a—1,07	e	b—1,10
Mo^{6+}	g—0,45a—0,65	e	e	e
Ti^{4+}	b—0,80	c—1,26	a—0,74	e
Ge^{4+}	a—1,36	b—1,44	b—1,55	b—1,38
W^{6+}	g—1,35a—1,44	e	e	f
Pd^{2+}	h—0,51	h—0,56	h—0,58	d
Sn^{4+}	b—1,29	c—1,44	g—1,41a—1,62	b—1,38
Sb^{3+}	b—0,63	b—0,72	a—0,75	d
As^{3+}	c—1,38	b—1,67	e	g—1,59
Sb^{5+}	d	a—0,78	b—0,84	b—0,75
Cd^{2+}	c—0,55	b—0,58	a—0,68	a—0,79
Cu^{2+}	a—0,14	b—0,33	b—0,39	g—0,16a—0,46
Tl^{+}	b—0,42	e—0,42	e—0,37	b—0,32
Zn^{2+}	e	g—1,18;—1,32	g—1,41;—1,57	a—1,30
V^{5+}	e	e	e	b—1,13
Mn^{2+}	e	c—0,83	a (Mn^{III})—0,14	a—1,70
UO^{2+}	e	a—0,55	a—0,60	b—0,60
Cr^{6+}	e	c—0,32	a—0,81	b—0,28
Sn^{2+}	e	e	e	e
As^{5+}	e	e	e	e
In^{3+}	e	e	e	e
Ce^{3+}	e	e	e	e
Ce^{4+}	e	e	e	e
Th^{4+}	e	e	e	e

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a) Good wave with a diffusion character, suitable for analytical use; b) clearly defined wave with a diffusion character; c) wave which is difficult to measure; d) precipitate formation; e) reduction could not be effected over the available potential range; f) beginning of hydrogen overvoltage (depressed); g) double wave; h) poorly developed double wave; only the approximate mean value of the half-wave potentials of both waves is given. The half-wave potentials were measured relative to the saturated calomel electrode. Ionic concentration $1\cdot10^{-3}$ M.

Nitrogen was used to purge oxygen from the solution before taking polarograms. It follows from the table that copper and thallium will interfere with the polarographic determination of manganese, since these elements are polarized in a potential region close to the half-wave depolarization potential of manganese; platinum and gold will also interfere since their waves precede the manganese wave.

Interference may also be shown by antimony, lead, and silver since they form precipitates in this medium, and the trivalent manganese in the form of its complex may be partially adsorbed by these precipitates. Elements which form complexes with sodium sulfosalicylate may also interfere since they depress the concentration of the sulfosalicylate in the supporting electrolyte. Accordingly in order to carry out an analysis the method of standard additions must be used.

The complex of divalent manganese with sulfosalicylic acid has been studied by Japanese research workers [7]. They used hydroxylamine hydrochloride for preventing the complex from being oxidized. The wave of the trivalent manganese complex studied in the work described in the present article is more suitable for analytical purposes because of the positive value of the half-wave potential.

Determination of manganese in siderites. A 0.2 g finely ground sample is dissolved in approximately 15 ml hydrofluoric acid and two drops of concentrated sulfuric acid contained in a platinum crucible; the mixture is heated to the appearance of white fumes. The residue in the crucible is dissolved in hot water and the solution quantitatively transferred to a 100 ml standard flask. Twelve g of sodium sulfosalicylate is added, and sodium hydroxide solution is added dropwise until an orange color appears. Sodium hydroxide is then added in sufficient amount to ensure that its final concentration in the solution in the standard flask is $5 \cdot 10^{-2}$ M. The volume of the solution is made up to the mark with water and the whole mixed. An aliquot of this solution is transferred to a Calousek cell, and after 3 min (after oxidation of the manganese complex by air) oxygen is purged from it by means of nitrogen; polarograms are taken starting at +0.1 v using anode-cathode polarization and a 2 v storage battery. The results are evaluated by the method of standard additions. Two different samples of siderite with contents of 2.06% and 1.92% manganese were analyzed in this way. The values found were 2.06% and 1.87% respectively.

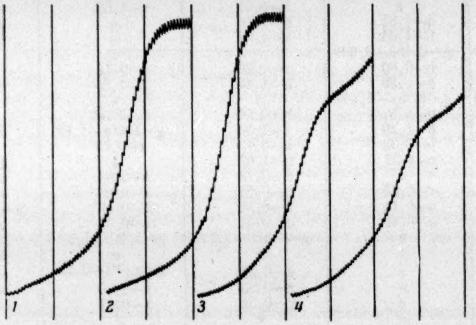

Fig. 1. Polarographic determination of manganese in siderites. Electrolyte: $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. 1) Sample; 2) ditto + 0.55 mg Mn; 3) sample; 4) ditto + + 0.55 mg Mn. Storage battery 2.0 v; S = 1/15, anode-cathode polarization (saturated calomel electrode); oxidation by air for 3 min; purging with nitrogen for 3 min.

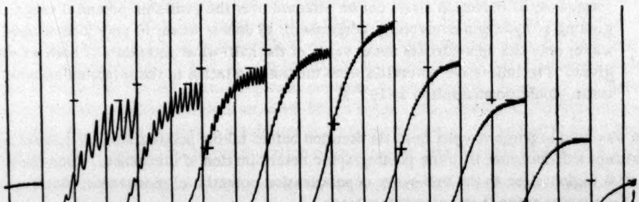

Fig. 2. Relation between wave height and manganese concentration, and between wave height and the height of the mercury reservoir. Electrolyte: $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. 1-5) $1 \cdot 10^{-3}$ M – $5 \cdot 10^{-3}$ M $MnCl_2$; 5-9) $5 \cdot 10^{-3}$ M $MnCl_2$; 5) h = 64 cm; 6) h = 49 cm; 7) h = 36 cm; 8) h = 25 cm; 9) h = 16 cm. Storage battery 2.0 v; S = 1/40; polarograms taken during anode-cathode polarization (saturated calomel electrode); oxidation by air for 3 min; purging with nitrogen for 3 min.

SUMMARY

The polarographic behavior of a number of ions in alkaline sulfosalicylate solutions has been studied, and a method has been developed for the rapid determination of manganese in mineral raw material. The reduction waves of a trivalent manganese complex were used.

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SPECTROPHOTOMETRIC DETERMINATION OF ULTRA-SMALL AMOUNTS OF NICKEL IN INDIUM

V. M. Peshkova, V. M. Bochkova, and E. K. Astakhova

M. V. Lomonosov Moscow State University

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Earlier [1] we suggested α-furildioxime, which permits determination of $5 \cdot 10^{-8}$ g or $5 \cdot 10^{-6}$% of nickel in one g of indium or aluminum, for determining nickel in high purity metals. In order to determine smaller amounts of nickel without increasing the weight of metal sample, it is obvious that one must use a reagent which gives a compound with a higher molar absorption coefficient with nickel.

TABLE 1. Molar Extinction Coefficients of Compounds of Nickel with Dioximes

Reagent	λ_{max}	ϵ_{max} [2]	ε*
α-Benzyldioximate	273	$4{,}03 \cdot 10^4$	$5{,}0 \cdot 10^4$ ($\lambda^* = 275$ mμ)
	361	$9{,}89 \cdot 10^3$	$1{,}0 \cdot 10^4$
	406	$1{,}09 \cdot 10^4$	$1{,}2 \cdot 10^4$
A-Furildioximate	293	$3{,}90 \cdot 10^4$	$5{,}0 \cdot 10^4$*
	384	$1{,}04 \cdot 10^4$	$1{,}0 \cdot 10^4$
	435	$1{,}52 \cdot 10^4$	$1{,}9 \cdot 10^4$

*ε-values were obtained by measuring the absorption of chloroform solutions of the nickel dioximates separated in the solid form.

As the results in Table 1 show, nickel dioximates have three absorption bands. Nickel α-benzyldioximate and nickel α-furildioximate absorb strongly in the ultraviolet. The reagents themselves, however, which are always taken in excess for the determination of nickel and are readily soluble in the extractants used, absorb in this spectral region.

We decided on α-benzyldioxime, since its compound with nickel is stable to the action of alkali, and, in contrast to the compound of nickel with α-furildioxime and the free reagent, can be removed from the extractant layer with a solution of sodium hydroxide (Fig. 1), so that measurements can be made at λ = 273 mμ (ε = 50,000).

EXPERIMENTAL

Reagents and apparatus. All the reagents and distilled water used were carefully purified both from possible traces of nickel and from materials which exhibit characteristic absorption at 275 mμ and which can be extracted by chloroform.

Nitric acid was purified by distillation in quartz apparatus. Commercial chloroform was purified by Weisberger's method [3].

Ethanol was distilled over solid sodium hydroxide; α-benzyldioxime was twice recrystallized from dioxane. All reagents were controlled for freedom from nickel by a spectrophotometric method.

The optical density of solutions was measured on a SF-4 spectrophotometer fitted with a hydrogen lamp, cylindrical teflon cells with quartz windows and having a capacity of 2.5 ml and a path length of 100 mm being used.

The vessels used were washed with distilled nitric acid and twice distilled water, since on using sodium carbonate and a chromic mixture for washing them, contamination was introduced which distorted the experimental results. Vessels which had not been previously used, as a rule, gave low and nonreproducible results.

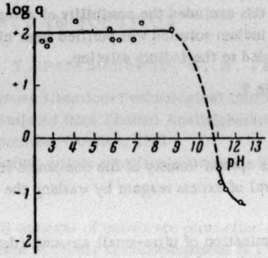

Fig. 1. The relation between the partition coefficient of α-benzyldioxime in the system H_2-CHCl_3 and the pH of the aqueous solution.

TABLE 2. Determination of Nickel in Indium (on a 1 g sample)

Nickel introduced μg	%	Found, μg	Error, %
0,010	$1\cdot10^{-6}$	0,010	0
0,010	$1\cdot10^{-6}$	0,010	0
0,020	$2\cdot10^{-6}$	0,022	+10
0,020	$2\cdot10^{-6}$	0,020	0
0,005	$5\cdot10^{-7}$	0,002	—60
0,005	$5\cdot10^{-7}$	0,003	—40
0,005	$5\cdot10^{-7}$	0,004	—20
0,005	$5\cdot10^{-7}$	0,005	0
0,005	$5\cdot10^{-7}$	0,0045	—10
0,005	$5\cdot10^{-7}$	0,006	+20

Mean arithmetic error ±16%.
Mean error of individual determinations ± 25%

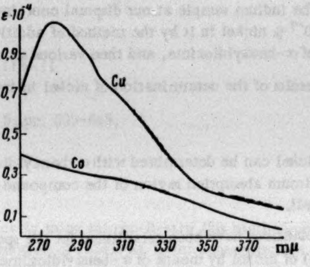

Fig. 2. Absorption spectra of metal α-benzyldioximates.

Conditions for determining nickel in solutions of its pure salts. Ultra-small amounts of nickel α-benzyldioximate (about 0.01 μg) are completely extracted at pH 8.0-11.3; larger amounts of nickel are extracted starting at a pH of 6.0 [4]. Completeness of extraction also depends on the ethanol concentration of the aqueous solution. The optical density is constant at ethanol concentrations not less than 20%. Variations in the ratio of the volumes of the aqueous and organic phase (from 2 to 8) do not affect the experimental results. There was very little difference between the results obtained when one and two extractions were used; accordingly, we always carried out only one extraction.

The optical density was measured relative to a solution obtained by extracting all the materials participating in the reaction (apart from nickel) with chloroform. Excess of reagent which is also extracted by chloroform and absorbs light at 275 mμ, was washed out with a sodium hydroxide solution.

Solutions of nickel α-benzyldioximate in chloroform conform to Beer's law over the concentration range 0.005 to 5 μg in 5 ml. The calibration line passes through the origin.

Cobalt and copper readily form extractable α-benzyldioximates which absorb light at 275 mμ (Fig. 2). It was established that on washing a chloroform solution of nickel, copper, and cobalt α-benzyldioximates with sodium hydroxide solution, the copper complex is completely destroyed, while three quarters of the cobalt complex is destroyed. In the case of commensurable amounts of Co and Ni, as is the case in high purity metals, the amount of cobalt which remains does not affect the experimental results.

Determination of nickel in indium metal. Under the conditions used for determining nickel, indium forms a hydroxide. Accordingly, citric and tartaric acids are added to the solution; these acids do not affect completeness of nickel extraction. One g of indium metal is dissolved in 10 ml of concentrated nitric acid contained in a quartz basin, and the solution evaporated almost to dryness. The solid residue is transferred to a separating funnel by means of 20 ml of a 20α citric acid solution and 5-10 ml of 20% potassium sodium tartrate.* Sodium hydroxide solution is then added until the pH is 8-11 according to indicator paper. Two ml of a 0.02% ethanol solution of α-benzyldioxime is then added, followed by ethanol until its concentration is not less than 20%. The contents of the funnel are shaken for 10-15 sec, and then extracted for 2 min with 5 ml of chloroform using a mechanical shaker. The aqueous layer is removed with a pipet. The chloroform solution is washed with two 5 ml portions of 1 N sodium hydroxide, each washing being carried out for 2 min. The optical density of the chloroform extract is finally measured at 275 mμ.

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* The use of tartrates alone or citrates alone invariably led to the formation of an amorphous precipitate at the pH used for extraction.

The indium sample at our disposal contained $2.8 \cdot 10^{-5}$ % nickel; this excluded the possibility of determining about 10^{-7} % nickel in it by the method of additions. Accordingly, the indium solution was purified from nickel by means of α-benzyldioxime, and then various amounts of nickel were added to the indium solution.

Results of the determination of nickel in indium are given in Table 2.

SUMMARY

Nickel can be determined with α-benzyldioxime by measuring the optical density of the compound formed in the maximum absorption region of the compound (275 mμ), after removal of excess reagent by washing the extract with alkali.

Conditions have been established for the spectrophotometric determination of ultra-small amounts (down to 0.005 μg) of nickel by means of α-benzyldioxime in solutions of its pure salts and in the presence of cobalt and copper.

A method has been developed for the determination of traces of nickel in indium metal down to a level of $5 \cdot 10^{-7}$ %; the reproducibility of the method is ±25%.

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A KINETIC METHOD FOR THE DETERMINATION OF MICROAMOUNTS OF COBALT IN SOLUTION

N. V. Parkhomenko, G. A. Prik, K. B. Yatsimirskii

Ivanovo Chemico-Technological Institute

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Small amounts of cobalt are most often determined photometrically using nitroso-R-salt; this method permits determination of cobalt at concentrations of 1-15 μg/ml [1]. For detection of cobalt at lower concentrations several kinetic methods have been suggested which are based on the catalytic effect of cobalt on the oxidation of various reducing agents by peroxides, and, in particular, of alizarin in alkaline media [2-5]. These methods are characterized by high sensitivity, and, as Bognar [4] has shown, permit detection of 0.000001 mg cobalt in 5 ml of solution. No method has, however, hitherto been developed for the quantitative determination of cobalt by kinetic methods. The work described here is an attempt to fill this gap.

EXPERIMENTAL

When alizarin is oxidized by hydrogen peroxide the colored material disappears, and, accordingly, the optical density of the solution changes as the reaction proceeds. At room temperature and in the absence of a catalyst, this reaction proceeds very slowly.

The reaction rate was studied on a FEK-N-54 photoelectric microcolorimeternephelometer using a cell with a path length of 3 cm and a No. 3 filter (effective wavelength 453 mμ), since solutions of alizarin in a borate buffer exhibit maximum absorption at 440-460 mμ. The solutions in the cell were thermostated at 25 ± 0.1 by continuous circulation of water from a thermostat through a special housing surrounding the cell.

Solutions of hydrogen peroxide and cobalt chloride, and the buffer solutions were prepared from the chemically pure preparations. Hydrogen peroxide concentration was determined iodometrically. Since there are no methods for the determination of low concentrations of cobalt, working solutions of cobalt were prepared by accurate dilution of the original stock solution of 0.1 M $CoCl_2$, the cobalt content of which was determined electrolytically.

The alizarin solution $C_{14}H_8O_4$ (1,2-dihydroxyanthraquinone) was prepared by dissolving 0.250 g of the recrystallized material [6] in 10 ml of 0.08 N NaOH, and subsequently diluting the volume to the mark with water in a 250 ml standard flask. The concentration of one of the alizarin solutions prepared was determined titrimetrically [6]. The concentration of the remaining solutions was controlled by means of their optical density.

Borate and veronal buffer solutions were prepared according to [7]. Twice distilled water was used for preparing all the working solutions.

Reaction mixtures were prepared in a 50 ml standard flask; alizarin solution, buffer solution, water for preliminary dilution, and hydrogen peroxide were introduced successively into the flask. The reaction mixtures were thermostatted at 25 ± 0.05° for 10-15 min. Catalyst solution was then added, followed by water to bring the volume up to the mark. A stopwatch was started off when the catalyst was added. The solution was carefully mixed and transferred to the thermostatted cell. Starting from the second minute after addition of the catalyst, the optical density of the solution was measured every minute for 10 min.

The final concentrations of the solutions were as follows: alizarin, $3.3\cdot10^{-5}$ M (D = 0.440 at 453 mμ in a 3 cm cell); hydrogen peroxide, $3.5\cdot10^{-2}$ M; cobalt chloride, $1.0\cdot10^{-8}$ to $11.2\cdot10^{-8}$ M; the pH of the solution was adjusted by means of borate or veronal buffers.

After treatment of the kinetic results obtained, the cobalt concentration of the solution was determined by the method described below. In order to check on the accuracy of the results obtained, experiments were carried out with a cobalt chloride solution labelled with Co^{60}. The concentration of the original cobalt chloride solution labelled with Co^{60} ($8.0 \cdot 10^{-5}$ M) was determined photometrically with nitroso-R-salt and the solution diluted accurately 100 times. Subsequently, in order to determine the cobalt content, the rate of the catalytic oxidation of alizarin at $CoCl_2$ concentrations ranging from $1.6 \cdot 10^{-8}$ to $11.2 \cdot 10^{-8}$ M was established, and the radioactivity of these same solutions measured on a 20 ml aliquot using a B-2 setup. The effect of foreign ions on the accuracy of cobalt determination was established. The effect of complex cobalt compounds on the rate of alizarin oxidation was also examined; these compounds included cobalt ethylenediammine, hexammine, and pentamminechloride. The experimental procedure was the same as that described above. Only the order in which the reagents were added was altered: hydrogen peroxide was added to the solution last. The stopwatch was started on adding the oxidizing agent.

DISCUSSION OF RESULTS

The rate of the catalytic oxidation of alizarin by hydrogen peroxide conforms to the equation*

$$\frac{dx}{dt} = \varkappa (a - x)\, bc, \tag{1}$$

where $\varkappa$ is the catalytic coefficient (the velocity constant of the catalytic reaction); $(\alpha - x)$, $\underline{x}$, $\underline{b}$, $\underline{c}$ are the current (at a given time) concentrations of alizarin, its oxidized form, cobalt chloride, and hydrogen peroxide respectively.

The current concentrations of H_2O_2 and $CoCl_2$ are almost equal to the initial concentrations, since a large excess of hydrogen peroxide is taken with respect to alizarin, while the concentration of the cobalt ion, as a catalyst, remains constant.

The initial and current concentration of alizarin are related to the optical density of the solutions in accordance with Beer's law:

$$D_0 = \varepsilon l a, \tag{2}$$

$$D = \varepsilon l (a - x), \tag{2a}$$

where D_0 is the optical density of the solution at the start; D is the optical density of the solution at a given moment; ϵ is the molar extinction coefficient; l is the path length.

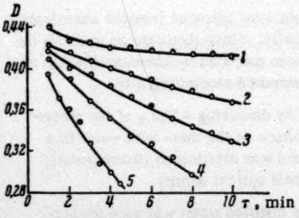

Fig. 1. Change of optical density with time during oxidation of alizarin at various $CoCl_2$ concentrations in the reaction mixture (M). 1) 0; 2) $1.3 \cdot 10^{-8}$; 3) $2.5 \cdot 10^{-8}$; 4) $5.0 \cdot 10^{-8}$; 5) $10.5 \cdot 10^{-8}$.

The change in optical density of an alizarin solution following upon its oxidation by hydrogen peroxide is shown in Fig. 1. Each curve characterizes the rate of reaction at a given cobalt ion concentration in solution. In order to get a linear relationship, it was found convenient during determination of cobalt by the kinetic method to integrate equation (1). After substituting the constants we get:

$$\lg \frac{a}{a - x} = \varkappa_1 bct. \tag{3}$$

Instead of the ratio of the initial alizarin concentration to its current concentration, the ratio of the optical densities corresponding to this ratio was substituted [equations (2) and (2a)], from this it was found that:

$$\lg D = -\varkappa_1 bct + \lg D_0. \tag{4}$$

The experimental results confirm the validity of this equation: the change in optical density with time when plotted in semilogarithmic coordinates is actually linear (Fig. 2). The slopes of these lines to the abscissa are proportional to the concentration of cobalt ions (b) at a constant H_2O_2 concentration (c):

$$\operatorname{tg} \alpha = \varkappa_1 bc. \tag{5}$$

In accordance with these equations, for determination of unknown concentrations of cobalt in solution, curves were constructed within the coordinates: cobalt concentration – tangent α (Fig. 3). When this is done all the experimental

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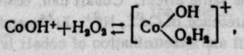
* The rate of the noncatalytic reaction is relatively low and can be disregarded.

points lie on a straight line. There is also a linear relation between tangent α and hydrogen peroxide concentration for a constant cobalt concentration [equation (5)]. This relation breaks down, however, at high H_2O_2 concentrations (higher than 0.02 M), as is evident from Fig. 4. Such a relation between tangent α and hydrogen peroxide concentration can be explained by the formation of a peroxide complex of cobalt according to the following scheme:



$$CoOH^+ + H_2O_2 \rightleftarrows \left[Co\begin{matrix}OH\\O_2H_2\end{matrix}\right]^+. \qquad (I)$$

the stability constant β of which is defined as

$$\beta = \frac{[Co(OH)(O_2H_2)^+]}{[CoOH^+][H_2O]_2]}. \qquad (6)$$

The concentrations of the complex compound, hydrogen peroxide, and total cobalt concentration are denoted respectively by C, c, and b. It follows from equation (6) that:

$$C_k = \frac{\beta b c}{1+\beta c}. \qquad (7)$$

Since the hydrogen peroxide concentration C is low, the value of αc is also low, and it can be disregarded, since the concentration of the complex compound of cobalt is proportional to the hydrogen peroxide concentration and the total cobalt concentration, then the reaction rate depends on H_2O_2 concentration. Under these conditions the reaction rate would be described by equation (3). On increasing the hydrogen peroxide concentration above 0.02 M, the value of αc increases and becomes appreciably greater than unity, and the denominator of the fraction in equation (7) can be replaced by βc (βc approximately equal to $\beta c + 1$). Equation (7) is simplified. This corresponds to the fact that almost all the cobalt has been converted into a complex compound:

$$C_k \approx b. \qquad (8)$$

Under these conditions there appears on the curve (Fig. 4) a horizontal section for which the kinetic equation:

$$\lg \frac{a}{a-x} = \varkappa_2 bt. \qquad (3a)$$

is valid. The slope of the straight lines $\log D_0/D - t$, in this case is equal to $\kappa_2 b$, the accuracy does not depend on the H_2O_2 concentration. The values of the catalytic coefficients calculated from the experimental results are equal, respectively to

$$\varkappa_1 = (3{,}1 \pm 0{,}7)\cdot 10^6 \frac{\text{liters}^2}{\text{moles}^2\cdot\text{min}} \text{ и } \varkappa_2 = (6{,}4 \pm 0{,}1)\cdot 10^5 \frac{\text{liters}}{\text{moles}\cdot\text{min}}$$

at pH = 9.24.

The relation between tangent α (for a constant H_2O_2 concentration higher than 0.02 M) and the pH of the solution is expressed by a curve which passes through a maximum (Fig. 5). This feature of the relation can be explained by the fact that alizarin and its compound with tetraborate, which dissociate like acids in three stages, obviously exhibit the highest catalytic activity in the second dissociation stage which occurs in the pH range 9.2-9.4.

The fact that alizarin interacts with tetraborate is confirmed by the absorption spectra of solutions of alizarin and of alizarin and tetraborate. In the case of alizarin solutions the absorption maximum lies at 520 mμ, while in the presence of $Na_2B_4O_7$ it shifts to 440-460 mμ.

A comparison of the radioactivity of solutions labelled with Co^{60} with their catalytic activity is made in Fig. 6. The linear relation between tangent α and the radioactivity, which is proportional to the cobalt concentration, shows that the two completely independent methods of determining cobalt give the same results.

Results for the determination of cobalt in pure solutions by the kinetic method are given in Table 1.

The effect of various impurities on the accuracy of cobalt determination was established. Examination of Table 2 shows that the presence of K^+, NH_4^+, VO_3, I^-, F^-, SO_4^{2-}, HO_2^-, CH_3COO^-, SCN^- ions at concentrations which are 10^5 times that of the cobalt, does not essentially affect the oxidation rate. In the presence of the heavy metal ions Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}, already at concentrations which are 100-1000 times the cobalt concentration, the rate of the catalytic reaction decreases approximately twice. Tartrates, citrates, and oxalates which complex cobalt show the same effect. Cobalt can, however, be determined in these cases by applying the requisite corrections. In the presence of Cd^{2+}, Ni^{2+}, Zn^{2+}, and sodium ethylenediaminetetracetate, the oxidation reaction hardly proceeds at all and determination of cobalt is impossible.

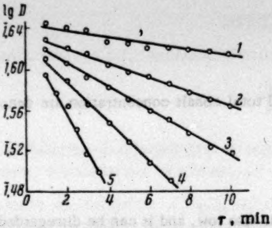


Fig. 2. Change of optical density with time, in semilogarithmic coordinates, during oxidation of alizarin at various $CoCl_2$ concentrations in the reaction mixture (M): 1) 0; 2) $1.3 \cdot 10^{-8}$; 3) $2.5 \cdot 10^{-8}$; 4) $5.0 \cdot 10^{-8}$; 5) $10.5 \cdot 10^{-8}$.

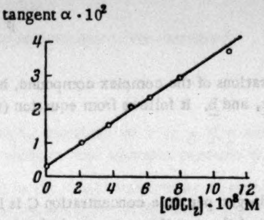


Fig. 3. The relation between the value of tangent α and cobalt concentration $[H_2O_2] = 5.2 \cdot 10^{-2}$ M; pH = 9.24; t = 25°.

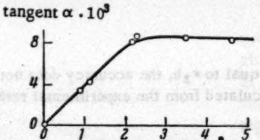


Fig. 4. The relation between the value of tangent α and hydrogen peroxide concentration $[H_2O_2] = 4.75 \cdot 10^{-8}$ M; pH = = 9.24; t = 25°.

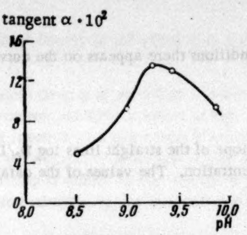
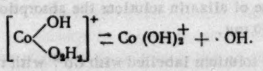


Fig. 5. The relation between the value of tangent α and pH of the solution. $H_2O_2] = 0.8 \cdot 10^{-2}$ M; $[CoCl_2] = 3.1 \cdot 10^{-6}$ M; t = 25°.

The following oxidation mechanism can be postulated to explain the catalytic action of divalent cobalt. The complex compound formed according to equation (I) can breakdown with formation of the hydroxyl radical OH and trivalent cobalt according to the scheme:



$$\left[Co\begin{matrix} OH \\ O_2H_2 \end{matrix}\right]^+ \rightleftharpoons Co\,(OH)_2^+ + \cdot OH. \qquad \textbf{(II)}$$

The catalyst is regenerated as a result of the reduction of Co^{III} by the hydrogen peroxide aniona:

$$Co(OH)_2^+ + O_2H^- \rightleftharpoons CoOH^+ + O_2H + OH^-. \qquad \textbf{(III)}$$

The perhydroxy radical $\cdot O_2H$, just like the $\cdot OH$ radical can oxidize alizarin. The products formed by the oxidation of alizarin with hydrogen peroxide in an alkaline medium could be: β [2-carboxy-1,4-diketonaphthyl-3] acrylic acid ($C_{14}H_9O_5$) and β [2-carboxy-1,4-diketonaphthyl-3] dihydroxyacrylic acid ($C_{14}H_{11}O_8$).

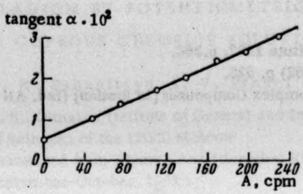


Fig. 6. Comparison of the radioactivity of $CoCl_2$ solutions labelled with Co^{60}, with their catalytic activity. $[H_2O_2] = 3.8 \cdot 10^{-2}$ M; pH = 9.24; t = 25°.

TABLE 1. Determination of Cobalt in Solution by the Kinetic Method

Cobalt taken, M × × 10^8	No. of expts.	Cobalt found by means of the calibration curve, M × 10^8	Mean deviation × 10^8
2,9	3	3,2	±0,2
3,9	3	4,2	±0,4
4,8	3	4,7	±0,4
5,8	3	6,2	±0,4
7,2	3	7,5	±0,4

Stable complex compounds of Co^{III} do not possess any appreciable catalytic activity. Thus cobalt ethylenediammine $Co(en)_3$ (instability constant $2.04 \cdot 10^{-49}$ [8]) does not affect the rate of alizarin oxidation, while the catalytic activity of the cobaltammines $Co(NH_3)_6^{3+}$ (instability constant $3.1 \cdot 10^{-33}$ [8]) and $Co(NH_3)_5^{2+}$ (instability constant $1.85 \cdot 10^{-6}$ [7]) is ten thousand times weaker than the activity of the free cobalt cation. Addition of ammonia to a solution containing a cobaltammine sharply depresses the catalytic activity.

TABLE 2. Effect of Foreign Ions on the Results of Cobalt Determination in Solution by the Kinetic Method

Foreign ion	Ratio of foreign ion concentration to cobalt concentration	Slope of the line to the abscissa · 10^{+2}	Foreign ion	Ratio of foreign ion concentration to cobalt concentration	Slope of the line to the abscissa · 10^{+2}
—	—	7,2	MoO_4^{2-}	$6,0 \cdot 10^4$	1,1
K^+	$1,0 \cdot 10^5$	7,2	WO_4^{2-}	$1,0 \cdot 10^4$	2,9
NH_4^+	$1,0 \cdot 10^5$	7,2	VO_3^-	$3,0 \cdot 10^3$	7,2
Ba^{2+}	$7,0 \cdot 10^3$	3,8	I^-	$2,0 \cdot 10^5$	7,2
Ca^{2+}	$4,0 \cdot 10^3$	3,3	F^-	$2,0 \cdot 10^5$	7,2
Mg^{2+}	$4,0 \cdot 10^3$	4,6	SO_4^{2-}	$2,0 \cdot 10^5$	7,2
Sr^{2+}	$2,0 \cdot 10^3$	4,6	SCN^-	$2,0 \cdot 10^5$	7,2
Cu^{2+}	$8,0 \cdot 10^3$	4,0	CH_3COO^-	$2,0 \cdot 10^5$	7,2
Cd^{2+}	$2,0 \cdot 10^3$	0	NO_2^-	$2,3 \cdot 10^5$	7,2
Ni^{2+}	$2,0 \cdot 10^3$	0	PO_4^{3-}	$2,0 \cdot 10^5$	6,3
Zn^{2+}	$1,5 \cdot 10^2$	0,2	Tartrate	$4,0 \cdot 10^4$	4,0
Pb^{2+}	$1,6 \cdot 10^3$	5,6	Citrate	$1,8 \cdot 10^4$	3,8
Mn^{2+}	$1,0 \cdot 10^3$	6,0	Oxalate	$1,9 \cdot 10^3$	2,1
Sn^{2+}	$5,3 \cdot 10^3$	7,0	Sodium ethylenediaminetetracetate	$1 \cdot 10^3$	0
Al^{3+}	$1,0 \cdot 10^3$	4,1			
Fe^{3+}	$1,0 \cdot 10^3$	3,1			
Gr^{3+}	$2,0 \cdot 10^3$	3,6			

SUMMARY

A study has been made of the catalytic oxidation of alizarin by hydrogen peroxide in an alkaline medium in the presence of cobalt salts. It has been established that the rate of this reaction is proportional to the cobalt and alizarin concentrations. A kinetic equation has been derived and a mechanism is postulated for the reaction studied.

Using the reaction studied a method has been developed for the quantitative determination of cobalt at concentrations of the order of 10^{-8} M.

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DETERMINATION OF PLATINUM IN THE PRESENCE OF PALLADIUM BY POTENTIOMETRIC TITRATION WITH A CUPROUS CHLORIDE SOLUTION

N. K. Pshenitsyn, I. V. Prokof'eva, and A. E. Bukanova

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy
of Sciences of the USSR, Moscow

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Chloroplatinates interact with Cu_2Cl_2 according to the equation: $PtCl^{2-} + 2Cu^{I} \rightleftharpoons PtCl_4^{2-} + 2Cu^{2+} + 2Cl^-$. Muller [1] was the first to make use of this reaction for the determination of platinum by potentiometric titration. Recently, research has been directed [2, 3] towards establishing the requisite experimental conditions more accurately, and at simplifying the technique of determining quadrivalent platinum quantitatively by titration with Cu_2Cl_2 solution.

The authors of these papers have observed that the nature of the titration changes and the accuracy with which platinum is determined decreases as the hydrochloric acid content of the solution increases. It was established that titration can be carried out both at room temperature, and on heating the solution to 50-70°, and that chlororhodiates do not interfere with platinum determination. Nevertheless, when chlororhodiates are present in solution, quadrivalent iridium is reduced and is titrated together with quadrivalent platinum with a common potential jump. Under certain conditions of temperature, acidity of solution, and ratio of chloroiridate and chloroplatinate concentrations in solution, two potential jumps are observed during titration: one corresponds to completion of reduction of Ir^{IV} to Ir^{III}, while the other corresponds to completion of reduction of Pt^{IV} to Pt^{III}.

Grinberg and Maksimyuk [3] have also shown that it is possible to determine quadrivalent platinum by titrating with a solution of Cu_2Cl_2 in the presence of the complex chlorides of divalent palladium. Published results relate to the determination of platinum in hydrochloric acid solutions of chloroplatinates, containing palladium in amounts approximately equal to or somewhat less than the platinum content.

When we tried to use potentiometric titration for the quantitative determination of platinum in solutions containing preponderant amounts of palladium, we came up against some difficulties which made it necessary to carry out an additional study of the effect of palladium on the character of the titration, and on the accuracy of platinum determination.

Reagents and apparatus. Our work was carried out on a synthetic mixtures prepared from solutions of chloroplatinic acid and sodium chloropalladiate of known concentration (about 1 mg/ml), containing hydrochloric acid (1-2%) and sodium chloride (up to 2%).

Cuprous chloride was prepared by the method recommended by Gregor [4] or the commercial material (analytical grade) was used. When the reagent was partially oxidized it was washed with a small amount of hydrochloric acid and water for removing $CuCl_2$.

Cu_2Cl_2 solution (0.01-0.03 N) in hydrochloric acid was prepared according to the method given in Grinberg's paper, and it was stored in a dark colored flask in a carbon dioxide atmosphere [2, 3]. The Cu_2Cl_2 solution was standardized against a standard solution of chloroplatinic acid. Potentiometric titration was carried out on a compensation setup with a type PPTV potentiometer and a galvanometer which permits the emf to be determined with an accuracy of 1 mv. A platinum wire or a gold disc was used as the indicator electrode, while a saturated calomel electrode was used as the reference electrode.

EXPERIMENTAL

The original solution containing platinum, or platinum and palladium, in the form of their complex chlorides, was evaporated carefully on a water bath to the moist salt state (sodium chloride should be present to prevent hydrolysis of palladium salts). The dry residue was dissolved in hydrochloric or sulfuric acid of a known concentration and the solution transferred to titration vessel. The volume of solution being titrated was 50 ml. CO_2 was passed through the liquid for 5-10 min before starting a titration in order to remove the air. Titration was carried out at room temperature while the solution was continuously stirred and the system was carefully isolated from atmospheric oxygen by means of CO_2.

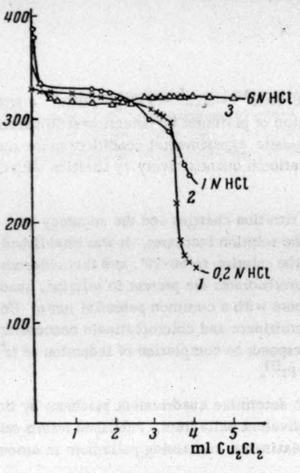

Fig. 1. Effect of hydrochloric acid concentration on titration of chloroplatinate with Cu_2Cl_2. 5.16 mg Pt taken. Theoretical amount of Cu_2Cl_2 that should be used 3.61 ml. Amount of Cu_2Cl_2 used for titration, ml: 1) 3.60; 2) 3.70; 3) not titrated. Pt found by titration, mg: 1) 5.15; 2) 5.29; 3) not determined.

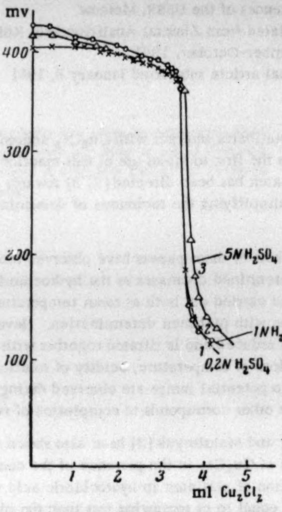

Fig. 2. Effect of sulfuric acid concentration on titration of chloroplatinate with Cu_2Cl_2 solution. 5.16 mg Pt taken. Theoretical amount of Cu_2Cl_2 that should be used, 3.61 ml. Amount of Cu_2cl_2 used for titration, ml: 1) 3.60; 2) 3.60; 3) 3.70. Pt found by titration, mg: 1) 5.15; 2) 5.15; 3) 5.20.

The experiments which we carried out confirmed that in solutions containing a smaller amount of palladium than platinum, the complex chlorides of quadrivalent platinum are titrated with a clearly defined potential jump at the equivalence point, while platinum is determined with the same accuracy as in pure solutions.

As the concentration of palladium increased with respect to that of platinum, the character of the titration curve for quadrivalent platinum changes in that the value of the potential jump at the equivalence point decreases, while in some instances no jump is observed at all.

In such cases, after reduction of quadrivalent platinum to its divalent state, deposition of metallic palladium (particularly in solutions < 0.1 N HCl) is sometimes observed; this may be a qualitative indication of the completeness of reduction of quadrivalent platinum. It was observed that when the palladium concentration exceeds the platinum concentration by an insignificant amount, a certain increase in the acidity of the solution being titrated enables reduction of palladium to its metallic form to be held back, and a potential jump to be observed during titration of platinum. Nevertheless, satisfactory results are only obtained for determination of platinum in solutions whose acidity does not exceed 1.0 N HCl (Fig. 1).

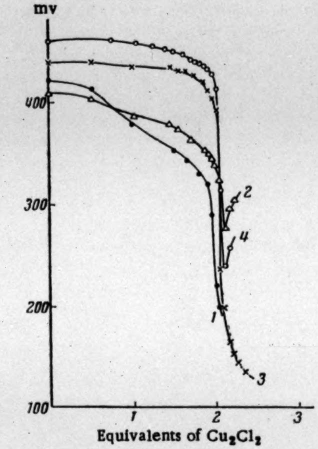

Fig. 3. Change in the value of the potential jump at the equivalence point as a function of the relative contents of Pt and Pd in solution, and of the material of the indicator electrode. 1) 3.10 mg Pt and 3.05 mg Pd taken. 1.99 equiv. Cu_2Cl_2 used. 3.08 mg Pt determined; 2) 3.10 mg Pt and 6.10 mg Pd taken. 2.04 equiv. Cu_2Cl_2 used. 3.16 mg Pt found; 3) 3.10 mg Pt and 3.05 mg Pd taken. 2.05 equiv. Cu_2Cl_2 used. 3.18 mg Pt found; 4) 3.10 mg Pt and 6.10 mg Pd taken. 2.05 equiv. Cu_2Cl_2 used. 3.18 mg Pt found.

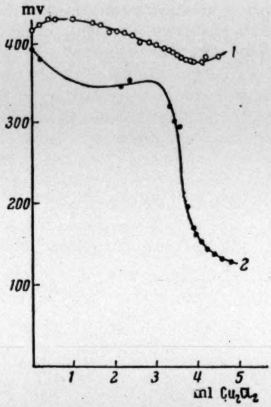

Fig. 4. The change in the character of the titration of chloroplatinate with Cu_2Cl_2 solution in the presence of palladium after addition of KI. 1) 5.16 mg Pt and 30.5 mg Pd taken. 1.0 N H_2SO_4 No KI present. 5.36 mg Pt found; 2) 5.16 mg Pt and 30.5 mg Pd taken. 1.0 N H_2SO_4. 5.9 ml of 0.1 N KI added. 5.22 mg found.

However, when the solution being titrated was acidified, not with hydrochloric acid, but with sulfuric acid, the character of the titration curve and the value of the potential jump hardly changed at all on changing the sulfuric acid concentration over a fairly wide range (Fig. 2). Neither did the presence of sodium chloride (up to 2%) affect the character and the results of the titration of chloroplatinates with Cu_2Cl_2 solution.

Table 1 contains results for the determination of platinum in pure solutions of chloroplatinates, and in solutions containing chloropalladiates as well, when the solutions were acidified with sulfuric acid.

Thus experiments have shown that in sulfuric acid solutions, quadrivalent platinum is titrated with a clearly defined potential jump at the equivalence point, and is determined with satisfactory accuracy.

Nevertheless, even in this case there is observed a change in the value of the potential jump at the equivalence point as a function of the pltainum and palladium contents in the solution (Fig. 3, curves 1 and 2).

It was observed that the value of the potential jump at the equivalence point depends to some extent on the material of the indicator electrode. Thus in the case of a gold electrode the potential jump is slightly higher (Fig. 3, curves 3 and 4) than when a platinum wire is used as the indicator electrode (Fig. 3, curves 1 and 2). But in this case, as in the other, the potential jump decreases as the palladium content increases with respect to platinum content in the solution being titrated, while the results for platinum determination show a tendency to increase. At a sufficiently high relative concentration of palladium in solution (e.g., Pt: Pd about 1: 6) the potential jump on the titration curve is almost unobservable (Fig. 4, curve 1).

In the case of solutions which contained considerably more palladium than platinum we succeeded in obtaining satisfactory results for pltainum by adding potassium iodide to the solution before titration. Despite the fact that chloroplatinate also reacts with potassium iodide [5, 6], as long as the solution contains palladium, precipitation of the latter as sparingly soluble PdI_2 occurs first. The palladium content of the solution is determined beforehand on a separate aliquot by titrating with KI according to a method suggested by Pshenitsyn and Ginsburg [7]. KI in the form of a 0.1 N solution is then added directly to the solution in the titration vessel in an amount which ensures precipitation of most of the palladium and leaves about 1 mg or less unprecipitated. This technique leads to a change in the ratio of the concentration of platinum to palladium such that there is more platinum than palladium, so that the platinum can be determined. It must be pointed out that excess potassium iodide should not be added, since in such cases the platinum will react with iodide ions and subsequent titration with Cu_2Cl_2 solution will not give satisfactory results.

TABLE 1. Determination of Platinum in the Presence of Palladium (0.02-0.05% NaCl. H_2SO_4 concentration from 0.2 N to 1 N. Platinum indicator electrode)

Taken		Pt found, mg	Error, mg	Taken		Pt found, mg	Error, mg
Pt, mg	Pd, mg			Pt, mg	Pd, mg		
8,4	—	8,4	0	5,4	3,0	5,3	—0,1
8,4	—	8,3	—0,1	6,5	3,0	6,6	+0,1
10,3	—	10,3	0	6,5	6,10	6,5	0
5,4	0,9	5,5	+0,1	10,3	10,4	10,3	0

TABLE 2. Determination of Platinum in the Presence of Preponderant Amounts of Palladium

Taken		Pt found, mg	Error, mg
Pt, mg	Pd, mg		
5,4	6,1	5,4	0
6,5	15,2	6,5	0
8,4	20,8	8,3	—0,1
5,4	30,5	5,5	+0,1
10,8	61,0	10,8	0

In Fig. 4 are shown titration curves of chloroplatinate in a solution containing chloropalladiate (Pt: Pt about 1: 6) to which no potassium iodide (curve 1) has been added, and after precipitation of most of the palladium with potassium iodide (curve 4).

Results of platinum determinations in the presence of palladium after precipitation of most of the latter with potassium iodide are given in Table 2. As these results show, the experimental error varies over the same limits as those observed during titration of pure solutions of chloroplatinates.

SUMMARY

It has been shown that the sulfuric acid content of solutions of chloroplatinate which are being titrated can be varied over a wide range, and that this variation in acidity does not affect the accuracy of platinum determination by titration with Cu_2Cl_2 solution.

As the palladium concentration of a solution increases with respect to platinum concentration, the potential jump on the titration curve decreases, and, in some cases, is not observed at all.

When chloroplatinates are titrated with Cu_2Cl_2 solution in the presence of palladium a greater potential jump is observed at the equivalence point when a gold electrode rather than a platinum electrode is used as indicator electrode.

On precipitating most of the palladium by adding KI directly to the titration vessel, it is possible to determine platinum in this solution, a clearly defined potential jump being obtained at the equivalence point.

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RAPID COMPLEXOMETRIC DETERMINATION OF BARIUM SULFATE IN BARYTA MINERALS

Ioan Dragusin*

Borzesti Chemical Combine (Rumania)

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Original article submitted October 31, 1960

The barium sulfate content of minerals is usually determined by the very cumbrous classical gravimetric method. This article is devoted to variants of a simple, rapid complexometric method which permit rapid determination of barium sulfate in minerals. The results obtained by this method agree with the results obtained by the classical method.

Complexometric method using alkaline fusion of the mineral. The method is based on dissolving barium sulfate in excess of a standard solution of sodium ethylenediaminetetracetate (EDTA-Na) and titrating excess of the latter with barium chloride solution.

A 0.2-0.25 g aliquot of finely ground baryta mineral is weighed in a platinum crucible, it is fused with a mixture of sodium and potassium carbonates, and the crucible plus the fused melt immersed in a beaker containing 100 ml of hot water, and the whole boiled for several minutes. Concentrated hydrochloric acid is added carefully until gas ceases to be evolved; a further 20-25 ml of acid is added together with 1-2 ml of 10% sulfuric acid. This leads to quantitative precipitation of barium sulfate in the form of fine particles, while all the remaining components of the mineral dissolved, and the silica remains in a colloidal form. The precipitate is filtered off and washed with hot water, the filter plus precipitate are transferred into a conical flask, and a small amount of distilled water added, followed by 25-30 ml of 0.1 N EDTA-Na; the whole is mixed while hot until a completely transparent solution is obtained [1].

Results of the Determination of $BaSO_4$ in Baryta Minerals

Sample No.	$BaSO_4$ content of the mineral, %		
	by the classical method	by the complexometric method	
		after alkali fusion	without alkali fusion
1	58.80	59.04	59.28
	58.94	59.11	59.32
	59.11	59.23	59.37
2	40.49	40.67	40.62
		40.46	
3	30.82	31.02	31.10
4	54.10	54.11	54.27
5	64.10	64.20	64.33

After the volume is diluted to 200-250 ml, 8-10 ml of concentrated ammonia is added, followed by 2-3 drops of an indicator solution of phthalein-complexon; excess EDTA-Na solution is then titrated with 0.1 N barium chloride solution. At the equivalence point the color of the solution changes sharply from a pale-rose to a bright-violet [2, 3].

A determination takes approximately 3 hr.

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* Translated from French by P. K. Agasyan.

The barium sulfate content is calculated by means of the formula:

$$\%\mathrm{BaSO_4} = \frac{(A-B)\cdot 0.0116713\cdot 100}{G}$$

where A is the number of ml of 0.1 N EDTA-Na used for dissolving the precipitate; B is the number of ml of 0.1 N barium chloride used for titrating excess EDTA-Na.

One ml of 0.1 N EDTA-Na corresponds to 0.0116713 g $BaSO_4$.

Complexometric method without alkali fusion. All operations are carried out directly on the untreated mineral, the alkali fusion operation being omitted.

Two-three ml of concentrated sulfuric acid is added to 0.2-0.25 g of mineral contained in a 100 ml beaker and the whole stirred with a glass rod. The mixture is heated for 2-3 min while stirring, until white fumes appear. The beaker is then cooled and 2-3 ml of distilled water carefully added, followed by 50-60 ml of hydrochloric acid (1:2) the mixture is boiled for 15 min and then allowed to stand for insoluble materials to settle out.

The insoluble residue is separated by decantation. The residue contains fine particles of barium sulfate, insoluble silica, and small amounts of calcium. The residue in the beaker is covered with a concentrated solution of ammonium carbonate and the whole stirred with a glass rod for 15 min until the calcium sulfate has changed into the carbonate. The mixture is then filtered, and the precipitate washed, first with a small amount of ammonium carbonate, and then with a hot, dilute solution of hydrochloric acid, and hot distilled water.

The filter plus precipitate containing barium sulfate and silica are transferred to a conical flask and treated with EDTA-Na solution as indicated above. The insoluble silica remains as a suspension. The solution is diluted to 200-250 ml and excess EDTA-Na titrated in an ammoniacal medium in the presence of phthaleincomplexon.

A determination takes about the same time as the first variant.

The results obtained by these variants are compared in the table with those obtained by the classical gravimetric method.

Reagents used: 1) 0.1 N EDTA-Na. 18.61 g of EDTA-Na and 3.8-3.9 g of sodium hydroxide (pellets) are dissolved in distilled water in a one liter standard flask and the volume made up to the mark with water. The solution is standardized complexometrically against 0.1 N standard barium chloride solution.

2) 0.1% Phthaleincomplexon solution. Twenty mg of the preparation is moistened with 1-2 drops of concentrated ammonia solution, after which it is diluted with 20 ml of distilled water. The solution does not keep for longer than a week.

SUMMARY

A rapid complexometric method is proposed for the determination of the barium sulfate content of baryta minerals; it is based on dissolving $BaSO_4$ in excess EDTA-Na solution, and titrating the excess with barium chloride solution in the presence of phthaleincomplexon.

A determination takes 3 hr; the results obtained are accurate and reproducible.

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DETERMINATION OF SULFUR, CHLORINE, AND FLUORINE IN BERYLLIUM OXIDE BY A SPECTROGRAPHIC METHOD

I. A. Berezin and K. V. Aleksandrovich

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Determination of small amounts of sulfur and halogens by spectrographic analysis is a very complex problem because their spectral lines, which are located in the visible and ultraviolet regions of the spectrum, and which can only be taken advantage of when special spectrographic apparatus is available, have high excitation potentials and are difficult to excite in a flame, arc, and spark. The sensitivity with which sulfur and the halogens can be determined, even in such powerful impulse sources as a condensed spark and a low voltage spark, does not exceed some hundredths of a percent [1-11]. Such sensitivity is not enough in a number of analytical problems, in particular for the determination of sulfur, chlorine, and fluorine in beryllium oxide. Methods recommended for the spectrographic analysis of beryllium oxide in which an electric arc is used [12-15] do not ensure the possibility of determining small amounts of sulfur and halogens either.

We have developed a technique involving the use of a hollow cathode which permits determination of thousandths of a percent of sulfur, chlorine, and fluorine in beryllium oxide.

McNally, Harrison, and Rowe [16] were the first to use a hollow cathode for determining sulfur and halogens; these authors, using the lines located in the infrared determined down to 1 μg sulfur, 0.2 μg chlorine, and 0.01 μg fluorine. Their method was developed further by Chaika [17] who determined ten thousandths of a percent of fluorine and thousandths of a percent of chlorine in uranium oxide and thorium oxide. Korovin and Lipis [18] have shown that a hollow cathode can be successfully used for the determination of many elements in metals having a high boilpoint. The advantages of a hollow cathode over other light sources for the determination of elements which are difficult to excite is explained by the simultaneous combination of high electronic and ionic temperature, discharge stability, low diffusion of the atoms from the discharge zone, and heating of the cathode material to the temperature necessary for evaporation of test material.

A schematic diagram of the vacuum setup which we used in our work is shown in Fig. 1.

The vacuum setup consists of evacuating and circulating systems. The air is pumped out with a RVN-20 prevacuum pump and a TsVL-100 oil diffusion pump. The vacuum is measured with a LT-2 thermoelectric tube. The discharge in the hollow cathode is carried out in an atmosphere of spectrographically pure helium which is introduced into the setup by means of a capillary tap [19]. The helium pressure is measured with an oil manometer. A DRN-10 mercury diffusion pump is used for circulating the helium. The helium is continuously purified during circulation of the gas, by means of a trap containing activated charcoal cooled with liquid air. Traps containing liquid nitrogen fitted in front of the diffusion pump are used for freezing out oil and mercury vapors.

When a hollow cathode is used, a considerable amount of time is taken up in pumping out the gas discharge tube. Moreover, when the tube is dismantled frequently, this being necessary for changing the electrodes, a considerable amount of helium is lost. Accordingly, we used a specially designed tube which enabled rapid replacement of electrodes without destroying the vacuum (Fig. 2). The molybdenum glass tube has two inlets made of molybdenum wire. Six molybdenum rods with a diameter of 1.2-1.5 mm are fused into the stopper of the tube; they are arranged around the periphery on which the hollow cathodes are fitted. The ground joint of the stopper is lubricated with a liquid vacuum grease which ensures free rotation of the stopper. Electrical contact between the hollow cathodes and the current supply is established by contact of the molybdenum rods with an elastic nickel disc fastened onto the lead-in made from molybdenum wire, fitted in such a way that it does not screen the light emitted by the hollow cathodes and does not hinder adjustment of the hollow cathodes.

The shape and dimensions of the cathodes are shown in Fig. 3. The choice of cathode material is of considerable importance. Cathodes of charcoal and graphite are completely unsuitable for analysis of oxides, since reduction reactions occur in the heated electrodes with formation of large amounts of carbon oxides whose presence in the discharge strongly depresses the sensitivity with which elements which are difficult to excite can be determined. At temperatures above 1000° the iron which starts to pass from iron and steel cathodes also lowers the accuracy and sensitivity of determination. It would be desirable to make cathodes from infusible metals: molybdenum, tantalum, or tungsten. Nevertheless preparation of such electrodes is associated with difficulties in the mechanical treatment of these materials. Good results can be obtained on using electrodes made from stainless steel the inner walls of such electrodes being protected with a tube of pure molybdenum.

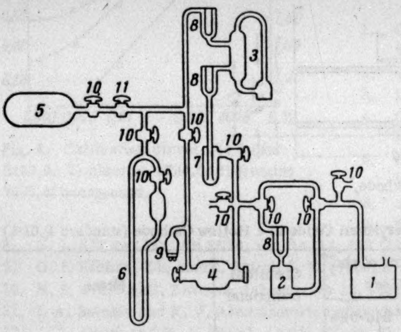

Fig. 1. Schematic diagram of the vacuum setup. 1) Prevacuum pump; 2) oil diffusion pump; 3) mercury diffusion pump; 4) tube plus hollow cathodes; 5) helium cylinder; 6) oil manometer; 7) trap with activated charcoal; 8) trap with liquid air; 9) manometer tube; 10) taps; 11) capillary tap.

Standards containing from 0.001 to 0.1% sulfur, chlorine, and fluorine are prepared from solutions of beryllium sulfate, beryllium chloride, and ammonium tetrafluoroberyllate, using pure beryllium oxide as the base. The standard samples are dried at 105-110° and are then ground up in an agate mortar.

Fifty mg samples of beryllium oxide are packed into the hollow cathodes. The discharge tube is evacuated to a pressure of $10^{-4} - 10^{-5}$ mm Hg and is then filled with helium to a pressure of 15 mm Hg. During the discharge process the helium is continuously purified by circulating it through the trap containing activated charcoal.

Spectra are photographed with an ISP-51 spectrograph fitted with a camera having $f = 270$. The slit width is 0.01 mm. The image of the hollow cathode is projected onto the slit by means of a one lens condenser.

The spectrograph casette is loaded with a composite plate such that the 4700-6000 A region is photographed on a "micro" type photographic plate, while the 6500-8000 A region is photographed on "Infra-760" type photographic plates. Before they are used the "Infra-760" plates are hypersensitized by immersing them for one minute in 5% aqueous ammonia and then drying them with a stream of air.

Two type UIP-1 rectifiers connected in series are used as the current source, the voltage of the rectified current being 1200 v. The current is regulated with a rheostat having a resistance of 6300 ohms and amounts to 300 μa. Exposure time is 2 min. At the end of this period sulfur and chlorine have "burnt out" completely; most of the fluorine also "burns out." (Table 1). The slower passage of fluorine into the discharge is explained by the fact that beryllium fluoride has a higher melting point and boiling point than beryllium sulfate and chloride.

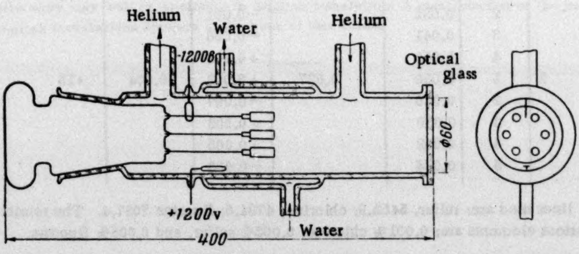

Fig. 2. Discharge tube.

The high stability of the discharge in the hollow cathode and the small background in the visible region of the spectrum enables calibration curves to be constructed for the determination of sulfur and chlorine in the coordinates (S, log C), where S is the absolute blackening of the spectral lines and C is the concentration of the element in the standards. Because of the continuous background in the infrared, the curve for determination of fluorine is constructed within the coordinates log $I_{\text{line + background}} - I_{\text{background}}/I_{\text{background}}$, log C), where $I_{\text{line + background}}$ is the intensity of the spectral line, $I_{\text{background}}$ is the background intensity, and C is the concentration (Fig. 4). In order to convert from blackening to intensity, use is made of the characteristic curve of the "Infra-760" photographic plate, constructed on the basis of the blackening marks.

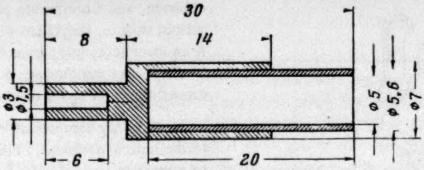

Fig. 3. Hollow cathode.

TABLE 1. "Burning Out" of Sulfur, Chlorine, and Fluorine from Beryllium Oxide in a Hollow Cathode (standard 0.01%)

Element	Spectral line, A	Difference between the blackening of the spectral line and the background, sec			Chemical compound	Notes
		0.120	120-240	240-360		
Sulfur	5453.9	0.71	–	–	$BeSO_4$	Decomposes at 550-600°
Chlorine	4794.5	0.66	–	–	$BeCl_2$	Boils at 520° (p = 760 mm Hg)
Fluorine	7037.4	0.38	0.20	–	$(NH_4)_2BeF_4$	On heating decomposes with formation of BeF_2 which melts at 800°

TABLE 2. Determination of Fluorine in Beryllium Oxide

Batch No.	Sample No.	Fluorine content, %	Mean value of the fluorine content, %	Absolute error, %	Mean absolute error, %	Mean absolute error, %
1	1	0.041	0.042	−0.001	±0.004	±9.5
	2	0.036		−0.001		
	3	0.041		−0.006		
	4	0.050		+0.008		
2	1	0.030	0.027	+0.003	±0.004	±15
	2	0.020		−0.007		
	3	0.030		+0.003		
	4	0.032		+0.005		
	5	0.024		−0.003		

The analytical lines used are: sulfur, 5453.9; chlorine, 4794.5; fluorine 7037.4. The sensitivities for the determination of the various elements are: 0.001% chlorine, 0.003% sulfur, and 0.005% fluorine.

Using this technique we have analyzed several batches of beryllium oxide. The fluorine content of two batches was determined (Table 2).

No sulfur and chlorine were found in the test samples. Accordingly, we checked on the reproducibility of the method by taking repeated photographs of standards. The mean relative error proved to be ±15-20%.

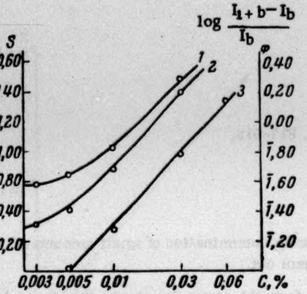

Fig. 4. Calibration curves. 1) Sulfur 5453.9; 2) chlorine 4794.5; 3) fluorine 7037.4/background.

SUMMARY

A method has been developed for the spectrographic determination of sulfur, chlorine, and fluorine in beryllium oxide by means of a hollow cathode. The method permits determination of 0.001% chlorine, 0.003% sulfur, and 0.005% fluorine in samples weighing 50 mg. The mean relative error is ± 15-20%.

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DETERMINATION OF SMALL AMOUNTS OF SULFUR IN TUNGSTEN AND MOLYBDENUM

Yu. N. Yurkevich and V. G. Shcherbakov

All-Union Scientific-Research Institute of Hard Alloys, Moscow

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The methods which are capable of giving the most reliable results during determination of small amounts of sulfur are those which require the minimum amounts of reagents to carry them out.

The combustion method would appear to be the most acceptable one from this viewpoint. Bruns, Braude, and Tsiklis[1] have suggested measuring the change in the concentration of the absorption solution on the basis of its electrical conductivity during carbon determination, and have extended this method to the determination of sulfur by absorbing the sulfur dioxide formed with hydrogen peroxide [2]. We have tried to determine sulfur by precipitating it in the form of barium sulfate.

It is impossible, however, to achieve a sufficiently high sensitivity by this method for the reliable determination of 0.0001% sulfur.

A considerable increase in the sensitivity with which sulfur can be determined is achieved by measuring the electrical conductivity when the sulfur dioxide is absorbed with an aqueous iodine solution. Under such conditions, for each atom of sulfur there appear in solution seven ions, four of which are hydrogen ions possessing an anomalously high mobility. Molecular iodine hardly dissociates at all into ions in water and does not increase the dissociation of water; accordingly, the electrical conductivity of the saturated solutions of iodine in water is determined mainly by the electrical conductivity of the water itself whose value is low.

The setup for sulfur determination is similar to the setup for carbon determination [1, 3, 4]. The modifications made to the setup in [4] involve the following:

a) the wash flask for absorbing sulfur dioxide was omitted; the combustion tube was connected through a tap with an absorption vessel which also acts as a measuring cell;

b) since even traces of moisture which condense on the cold parts of the apparatus almost completely absorb sulfur dioxide, the oxygen passing into the combustion tube must be dried. For this purpose a U-shaped tube containing calcium chloride was fitted between the combustion tube and the wash vessel containing alkali.

Firstly, we checked on the proportionality between the change in electrical conductivity and sulfur content. For this purpose the requisite amount of $ZnSO_4$ was calcined at a temperature of 1200°. Zinc sulfate was placed in the form of a solution in a boat; the solution was then evaporated in a drying oven. The curve shown in the diagram was obtained in this way.

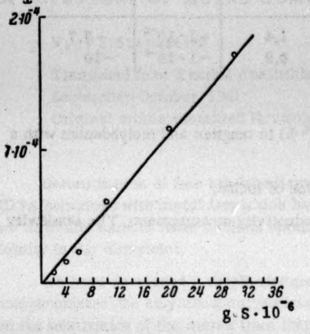
The sensitivity of the method amounts to 0.2-0.3 μg sulfur. It depends mainly on the accuracy with which the electrical conductivity is measured. This same curve served further as a calibration curve for determination of sulfur in tungsten and molybdenum.

Tungsten was examined first, because fewer difficulties arise when this metal is used. Tungsten is readily oxidized and lumps of metal can be used for analysis. In addition, the tungsten trioxide formed at the combustion temperature is sparingly volatile, so that there is no need for any after charge. Before taking samples the lumps of tungsten were carefully washed with acetone and dried. Two-three g of tungsten was placed in a quartz boat calcined beforehand in an oxygen stream at a temperature somewhat higher than the combustion temperature.

Boat plus sample were then placed in the cold zone of the combustion tube; the tube was sealed and purged with an oxygen stream for 30 min. During this period the measuring cell was washed several times with a saturated solution of iodine in water. The iodine solution was prepared by taking 5 g of iodine per liter of twice distilled water and dissolving it over a period of several days by periodic shaking. Six ml of the iodine solution (this amount of iodine solution was sufficient to cover the electrodes and bubbler tube completely in the cell which we used) was introduced into the measuring cell. The cell was placed in a thermostat in which it was kept for 15 min at 25°, and connected to the combustion system. Oxygen was then passed through the solution (5 min) and the first measurement of electrical conductivity made; the tap between the measuring cell and the combustion tube was closed, and an oven heated to 1200° fitted onto the tube. Completion of oxidation of the aliquot was followed by means of a rotameter (the level in the rotameter should be at the same position as it was before combustion). When combustion was complete the tap was opened again; the oxygen containing the sulfur dioxide was passed through the measuring cell for 30-40 min, and the electrical conductivity measured again. Measurements were repeated every 10 min. Absorption was regarded as complete when the electrical conductivity of the solution did not change over a period of 10 min.

After determination of sulfur in one sample of tungsten, standard zinc sulfate solution was added to an equal aliquot of sample and the total amount of sulfur determined. The results obtained are given in Table 1. They show that the method gives satisfactory results.

The method suggested permits determination of $1 \cdot 10^{-4}$ % of sulfur in tungsten with reasonable accuracy.



Relation between increase in electrical conductivity of the iodine solution and the amount of SO_2 absorbed.

During oxidation of molybdenum, molybdenum trioxide is formed; the latter completely evaporates at the combustion temperature and blocks up the tube. Consequently, before combustion, it is necessary to add zinc oxide which forms a sparingly volatile compound with molybdenum trioxide. When insufficient zinc oxide is added the readily fusible ternary compound of zinc oxide with quartz and molybdenum trioxide is formed, as a result of which the combustion tube becomes useless (fuses). Zinc oxide should therefore be added in a 4-5 fold excess. The boiling point of molybdenum trioxide is about 1160°, as a result of which the sublimation rate is high at 1200° and the trioxide does not succeed in reacting with the zinc oxide. To avoid this phenomenon, the oven temperature was gradually raised from 900 to 1200°. The remaining details of the method for the determination of sulfur in molybdenum are the same as those used for determination of sulfur in tungsten.

TABLE 1. Determination of Sulfur in Tungsten Metal after Addition of $ZnSO_4$. (The following sulfur contents were found for the W taken: $1.4 \cdot 10^{-4}$; $1.6 \cdot 10^{-4}$; $1.1 \cdot 10^{-4}$; $1.2 \cdot 10^{-4}$; $1.5 \cdot 10^{-4}$% S; mean value $1.4 \cdot 10^{-4}$% S)

Sample	S content (g) in an aliquot $\times 10^{-6}$	S added in (g) $\times 10^{-6}$	Amount of S that should be present (%) $\times 10^{-4}$	S found (%) $\times 10^{-4}$	Deviation (%) $\times 10^{-5}$	Error (%), relative
W + $ZnSO_4$	3.5	2	2.2	1.7	−5	−22.7
W + $ZnSO_4$	3.7	2	2.1	2.2	+1	+ 4.7
W + $ZnSO_4$	4.1	2	2.0	2.3	+3	+13
W + $ZnSO_4$	4.3	2	2.0	1.9	−1	− 5

It follows from Table 2 that the relative error is about 20%. The accuracy for the determination of sulfur in molybdenum is lower than in the case of tungsten, and is strongly dependent on the quality of the zinc oxide. Finally we analyzed two batches of molybdenum for their sulfur content. The amount found in the first bath was $3 \cdot 10^{-5}$; $3 \cdot 10^{-5}$; $1 \cdot 10^{-5}$; $5 \cdot 10^{-5}$% S, while in the second it was $5 \cdot 10^{-5}$% S.

The sulfur content of molybdenum samples analyzed was less than $1 \cdot 10^{-4}{}_{1}$, and in some cases was within the limits of experimental error.

TABLE 2. Determination of Sulfur in Molybdenum Metal (The following sulfur contents were found for the W taken: $4 \cdot 10^{-5}$; $2 \cdot 10^{-5}$; $2 \cdot 10^{-5}$; $6 \cdot 10^{-5}$; $6 \cdot 10^{-5}$; $3 \cdot 10^{-5}$; $4 \cdot 10^{-5}$% S; mean value $4 \cdot 10^{-5}$% S)

Sample	Sulfur content (g) × 10^{-6}	S added (g) × 10^{-6}	S content (%) × 10^{-4}	S found (%) × 10^{-4}	Deviation %	Error (%), relative
MO – 89 + $ZnSO_4$	0.9	2	1.3	1.4	$+1 \cdot 10^{-5}$	+7.7
MO – 89 + $ZnSO_4$	1.2	2	1	0.9	$-1 \cdot 10^{-5}$	–10

SUMMARY

Methods have been developed for the determination of sulfur ($1 \cdot 10^{-4}$ %) in tungsten and molybdenum with a relative error not greater than 20%.

The sulfur dioxide formed is absorbed with a saturated aqueous solution of iodine.

The concentration of the ions formed is determined by electrical conductivity measurements. The sensitivity of the method is 0.2–0.3 μg sulfur.

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DETERMINATION OF ETHYLENEDIAMINETETRACETIC ACID IN SOLUTIONS OF METAL COMPLEXONATES

V. V. Starostin

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Determination of free ethylenediaminetetracetic acid (EDTA) is readily carried out; methods for determining EDTA combined with metal ions which have been described in the literature [1-3] cannot be used universally and are difficult; some of these methods require expensive and not readily available apparatus for measuring optical density in the ultraviolet.

We have developed a simple titrimetric method for the determination of EDTA in solutions containing the complexonates (the ethylenediaminetetracetates) of Fe^{III}, Fe^{II}, Al, Cu^{II}, Ni, Mn^{II}, Cr^{III}, Mg, and Ca which is based on the substitution of the metals from their complexonates by trivalent bismuth which forms a complexonate which dissociates to a lesser extent:

$$[MeEDTA]^{4-n} + Bi^{3+} \rightleftharpoons [BiEDTA]^{-} + Me^{n+}$$

Calculation shows that the equilibrium of this reaction is shifted almost completely toward the right hand side when pK_{MeEDTA} is less than pH_{BiEDTA}, if only by 3 units.

Bismuth complexonate is very stable in acid media; apparently, pK_{BiEDTA} is close to 25. Of the complexonates of the metals listed above, iron (III) and chromium (III) complexonates (pH = 25.0 and about 24 respectively) will not react with excess Bi^{3+} ions. Excess bismuth ions can be back titrated with solution of sodium ethylenediaminetetracetate (EDTA-Na) in an acid medium in the presence of xylenol orange [4, 5] or pyrocatechol violet [2].*

In the work described here we used 0.01 M solutions of $Bi(NO_3)_3$ and EDTA-Na. Xylenol orange was used as indicator.

It was established that in an acid medium (pH about 1) the reaction indicated above proceeds almost quantitatively in the cold in approximately 20 min, and on boiling in 1 min, for all the metal complexonates apart from those of iron (III) and chromium (III). Many complexonates react almost instantaneously.

In the presence of a reducing agent (ascorbic acid) ferric complexonate breaks down to form bismuth complexonate and Fe^{2+} ions. Under these conditions, chromium (III) complexonate hardly interacts at all with bismuth ions. Excess Bi^{3+} was backtitrated with EDTA-Na solution at pH 1-1.5; the color change of the indicator from raspberry to yellow was readily observable.

Experiments showed that EDTA can be determined with satisfactory accuracy even in the presence of large amounts of ions of various metals (Table 1).

TABLE 1. Determination of EDTA in Solutions Containing Various Metal Ions

Metal (10 mg taken)	EDTA, mg		Error, % (relative)
	taken	found	
Fe^{II}	14,25	14,25	0,0
Fe^{III}	14,25	14,20	—0,3
Al	14,25	14,30	+0,3
Ni	14,25	14,25	0,0
Cu	14,25	14,15	—0,7
$Fe^{II} + Fe^{III} + Al + Cu + Ni + Mn^{II} + Ca + Mg$ (10 mg each)	8,8	8,7	—1,1
	14,25	14,2	—0,3
	17,0	16,9	—0,6
	28,5	28,3	—0,8

The method recommended for the determination of EDTA is described below.

An aliquot of test solution containing 30-60 mg EDTA is introduced into a titration flask and acidified with 5 ml of $HClO_4$ (1 : 1). After adding 15-25 ml of 0.01 M $Bi(NO_3)_3$ solution the solution is heated to 90-100°. Ascorbic acid is added (0.6-1.0 g) and the solution allowed to stand for 10 min without heating; it is then diluted to about 100 ml with distilled water. A few drops of xylenol orange solution is added and excess bismuth titrated with 0.01 M EDTA-Na solution until the color changes from raspberry to yellow.

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* Presumably hematoxylin and gallein [6] could also be used for this purpose.

S^{2-} ions interfere since they form an insoluble sulfide with bismuth, accordingly they should be removed, e.g., by precipitation with $CuSO_4$.

For determination of EDTA combined with chromium (III) we used a well-known photometric method (measurement of the optical density of solutions of the violet chromium (III) complexonate at 550 mμ) [7, 8]. The pH of the solution being analyzed is adjusted to 3.5-4 according to universal indicator paper by addition of ammonia or sulfuric acid; in order to stabilize the solution EDTA-Na (25 mg/ml) was introduced in addition. The presence of free Cr^{3+} ions in solution, in addition to the chromium complexonate, does not lead to high results, since EDTA-Na and Cr^{3+} react very slowly in the cold. The colored complexonates of copper and nickel, as long as their contents are not too high (Cu, Ni : Cr $\leq$ 2), do not interfere with the determination since they absorb light strongly at other wavelengths.

Interference from large amounts of iron (III) complexonate is eliminated by addition of a strong reducing agent, e.g., sodium hydrosulfite; should elemental sulfur separate out, the solution is filtered through a fine filter paper.

The chromium complexonate concentration of a sample is determined by means of a calibration curve.

Table 2 contains results of the determination of EDTA in the presence of chromium (III) and other metals.

TABLE 2. Determination of EDTA Combined with Metal Ions

EDTA introduced into the solution,* g/liter	EDTA found in solution, g/liter			Error, % relative
	combined with chromium (photometric method)	combined with other metals (backtitration of excess bismuth)	Total	
1.00	0.63	0.38	1.01	+1.0
3.50	0.73	2.76	3.49	−0.3

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* The solution contained 1 g each of Fe and Al per liter; 0.5 g each of Mn, Ca, and Mg per liter; 0.1-0.15 g per liter of Cr; 0.1 g each of Cu and Ni per liter, in the form of their sulfates.

In conclusion the author would like to thank V. F. Luk'yanov for the valuable advice given in the course of this work.

SUMMARY

A titrimetric method is suggested for the determination of ethylenediaminetetracetic acid in the presence of the most common metal ions; it is based on back titration of excess bismuth ions with EDTA-Na in an acid medium in the presence of xylenol orange.

EDTA combined with chromium (III) is determined by measuring the optical density of solutions of chromium (III) complexonate.

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QUANTITATIVE DETERMINATION OF SOME IMPURITIES IN TITANIUM TETRACHLORIDE BY INFRARED SPECTROSCOPY

D. I. Tsekhovol'skaya and T. A. Zavaritskaya

All-Union Aluminum-Magnesium Institute, Leningrad

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Titanium tetrachloride used for metallurgical purposes should be purified as much as possible from all impurities it may contain. In order to organize and improve a purification technique it is essential to have methods for the quantitative determination of compounds which contaminate titanium tetrachloride. In work carried out earlier we demonstrated the possibility and expediency of using infrared absorption spectroscopy for the determination of such impurities as $TiOCl_2$, $VOCl_3$, HCl, C_6Cl_6, $COCl_2$, CO_2, CCl_3COCl [1-2] in titanium tetrachloride. The work described in the present article is a continuation of the study of the molecular nature of the impurities in technical titanium tetrachloride, and is devoted to development of quantitative methods for their determination.

Determination of thionyl chloride. An absorption band with ν = 1241 cm^{-1} is observed in the infrared absorption spectrum of technical titanium tetrachloride and in that of some cases of purified titanium tetrachloride. As experiment has shown, this band belongs to thionyl chloride and corresponds to the valence vibration of the $S=O$ group [3].

The band at ν = 1241 cm^{-1} could be chosen as an analytical band for the quantitative determination of thionyl chloride in titanium tetrachloride. However, it must be borne in mind that determination based on this band is possible only when the titanium tetrachloride does not contain appreciable amounts of such impurities as silicon tetrachloride with an absorption band at ν = 1222 cm^{-1} and phosphorus oxychloride with a band at ν = 1226 cm^{-1} and ν = 1264 cm^{-1}, as well as thionyl chloride. Accordingly, infrared spectroscopy can be expediently used for the determination of the thionyl chloride concentration of purified titanium tetrachloride which contains only very small amounts of silicon tetrachloride and phosphorus oxychloride.

We constructed a calibration curve relating optical density to the concentration of the impurity in standard solutions [4]. For this purpose, the absorption spectra of solutions with the following concentrations were taken: 0.005, 0.01, 0.02, 0.037, and 0.05%. As Fig. 1 shows, the calibration curve is linear; accordingly, the solutions conform to Beer's law over the concentration range examined. Each point on the curve is the mean of three measurements. The absorption coefficient calculated from the curve is equal to K = 150 cm^{-1} (when the concentration is expressed in % wt.) or K = 1040 liter/mole cm (concentration expressed in mole/liter/cm.

Thus in order to determine thionyl chloride in titanium tetrachloride, it is necessary to measure the optical density at the maximum of the band ν = 1241 cm^{-1}, and, knowing the coefficient, to calculate the concentration required by means of the formula:

$$c = D/Kd,$$

where c is the concentration, D is the optical density, and d is the path length.

The sensitivity of the determination is $1 \cdot 10^{-4}$% (wt.). The relative experimental error does not exceed 3-7%.

Determination of carbon disulfide. During a study of the infrared spectra of many samples of technical titanium tetrachloride, and intense band at ν = 1520 cm^{-1} was observed; this was shown experimentally to belong to carbon disulfide. This band can be used for analytical purposes since it is almost always free from overlapping by the absorption bands of other impurities and from those of titanium tetrachloride itself. Carbon disulfide is miscible with titanium tetrachloride in all proportions [5] and does not interact with it. This is confirmed spectroscopically, since the absorption band of pure carbon disulfide differs very little from the band observed in the spectrum of a solution of this compound in titanium tetrachloride.

For quantitative determination of carbon disulfide, a calibration curve (Fig. 2) was constructed using standard solution with the following concentrations: 0.0011; 0.0055; 0.0108; 0.0205 and 0.0303% (wt.). Each point on the curve is the mean of three measurements. The absorption coefficient determined from the curve is given by K = 780 cm^{-1} or K = 3450 liter/mole cm.

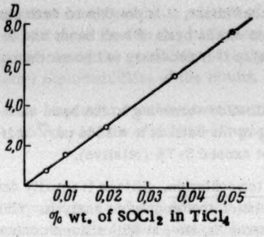

Fig. 1. Calibration curve for the determination of $SOCl_2$ in $TiCl_4$ on the basis of the band at ν = 1241 cm^{-1}.

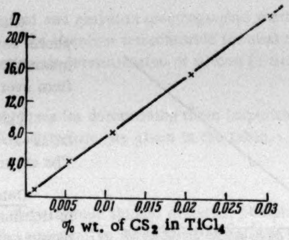

Fig. 2. Calibration curve for the determination of CS_2 in $TiCl_4$ on the basis of the band at ν = 1520 cm^{-1}.

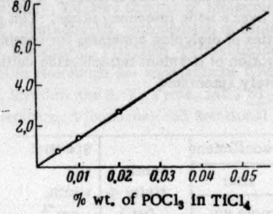

Fig. 3. Calibration curve for the determination of $POCl_3$ in $TiCl_4$ on the basis of the band at ν = 1226 cm^{-1}.

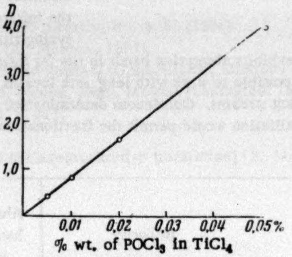

Fig. 4. Calibration curve for the determination of $POCl_3$ in $TiCl_4$ on the basis of the band at ν = 1264 cm^{-1}.

The sensitivity of the determination is $7 \cdot 10^{-6}$%; the relative experimental error does not exceed 3-7%.

Determination of phosphorus oxychloride. Two absorption bands with ν = 1226 cm^{-1} and ν = 1264 cm^{-1} were detected in the spectra of some samples of technical titanium tetrachloride. Chemical analysis of titanium tetrachloride showed the presence of small amounts of phosphorus. Experiments showed that the same two bands are observed in the infrared absorption spectra of a solution of phosphorus oxychloride in titanium tetrachloride. One absorption band at ν = 1295 cm^{-1} is observed in the spectrum of pure phosphorus oxychloride. This band is absent in the spectrum of a solution of phosphorus oxychloride in titanium tetrachloride while the other two bands at ν = 1226 cm^{-1} and ν = 1264 cm^{-1} appear. This testifies to an interaction between phosphorus oxychloride and titanium tetrachloride. There are published references [6-7] to the fact that on adding phosphorus oxychloride to titanium tetrachloride, the compound $POCl_3 \cdot TiCl_4$ is formed; this compound is limitingly soluble in titanium tetrachloride. Accordingly, the two bands observed at ν = 1226 cm^{-1} and ν = 1264 cm^{-1} can, presumably, be ascribed to the complex $POCl_3 \cdot TiCl_4$. It should be pointed out that the boiling point of this compound is 140°, which excludes the practical use of fractional distillation for purifying titanium tetrachloride (b. p. 136°) from phosphorus oxychloride. Both the bands with ν = 1226 cm^{-1} and ν = 1264 cm^{-1} can be used as analytical bands; these bands can be used for quantitative determination in those cases where the titanium tetrachloride only contains negligible amounts of such impurities as silicon tetrachloride and thionyl chloride. Analysis of technical titanium tetrachloride for its phosphorus oxychloride content is best carried out on the basis of the band at ν = 1264 cm^{-1}, which is more free from overlapping by other bands.

Standard solutions with varying contents of phosphorus oxychloride were prepared for the quantitative determination of the latter: 0.005; 0.010; 0.020; 0.051 % (wt.). Calibration curves constructed for the two analytical bands are shown in Figs. 3 and 4. The absorption coefficient for the band at ν = 1266 cm^{-1}, as determined from the curve and calculated on the basis of the $POCl_3$ molecule is 80 cm^{-1} or 715 liter/mole cm. The absorption coefficient for the band at ν = 1264 cm^{-1} is equal to 139 cm^{-1} or 1250 liter/mole cm.

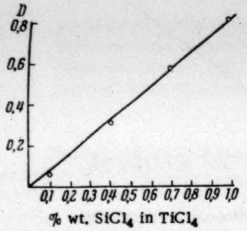

Fig. 5. Calibration curve for the determination of $SiCl_4$ in $TiCl_4$ on the basis of the band at 1222 cm^{-1}.

Knowing the absorption coefficient, it is possible to determine the phosphorus oxychloride concentration on the basis of both bands and to take the mean. In the case of band overlap it is necessary to choose the one more free from overlapping.

The sensitivity of determination according to the band at ν = 1226 cm^{-1} is $1.6 \cdot 10^{-4}$ %, while according to the band at ν = 1264 cm^{-1} it is $1 \cdot 10^{-4}$ %. The experimental error does not exceed 3-7% (relative).

Determination of silicon tetrachloride. Silicon is usually determined in titanium tetrachloride by emission spectrographic analysis. This method requires careful preparation of samples, and, at high silicon contents of the titanium tetrachloride (> 0.1%) gives a large error. It became necessary therefore to develop infrared spectroscopic method for the determination of silicon tetrachloride in titanium tetrachloride. This method permits the reproducibility of the results, and the accuracy with which silicon can be determined in technical titanium tetrachloride to be improved. In addition, the infrared method makes it possible to develop continuous methods for analyzing titanium tetrachloride for its content of this impurity. Titanium tetrachloride exhibits absorption bands in the far infrared and is transparent over a wide frequency range. This means that it is possible to work with long path lengths and opens up possibilities of designing apparatus for continuous control of plant streams. Continuous determination of the silicon concentration of titanium tetrachloride during its fractional distillation would permit the fractionation column to be completely automated.

Impurity	Absorption band, cm^{-1}	Absorption coefficient		Sensitivity % (wt.)	Spectral slit width, cm^{-1}
		cm^{-1}	liter / mole cm		
Thionyl chloride $SOCl_2$	1241	150	1040	$1 \cdot 10^{-4}$	6.6
Carbon disulfide CS_2	1520	780	3450	$7 \cdot 10^{-6}$	8.9
Phosphorus oxychloride $POCl_3$	1226	80	715	$1.6 \cdot 10^{-4}$	6.6
Silicon tetrachloride	1264	139	1250	$1 \cdot 10^{-4}$	6.6
Silicon tetrachloride $SiCl_4$	1222	0.807	8.0	$2 \cdot 10^{-2}$	

Silicon tetrachloride has the following fundamental vibration absorption bands: 150; 220; 425; 607 cm^{-1} [8]. The band at ν = 607 cm^{-1} can be observed when a KBr prism is used. Analysis of titanium tetrachloride for most of the impurities it contains is carried out over the region in which NaCl and LiF prisms are transparent. Work with a spectrometer fitted with a KBr prism presents certain experimental difficulties and requires additional study. All this complicates control of the quality of titanium tetrachloride under production conditions. It should also be pointed out that prism resetting also takes some time. We accordingly chose the band at 1222 cm^{-1} which belongs, apparently, to the first overtone of the frequency at ν = 607 cm^{-1}. The sensitivity of a determination based on this band is low, but it is still sufficient for the determination of silicon in technical titanium tetrachloride. For constructing a calibration curve (Fig. 5) standard solutions of silicon tetrachloride in titanium tetrachloride were prepared with the following concentrations: 0.10; 0.40; 0.70 and 0.99% (wt.). Each point on the curve is the mean of three measurements. The absorption coefficient found from the curve was K = 0.807 cm^{-1} or K = 8.0 liter/mole cm.

During determination of silicon tetrachloride one must take into account the possibility of overlapping from the bands of titanium oxychloride ν = 1184 cm^{-1}, thionyl chloride ν = 1241 cm^{-1}, and phosphorus oxychloride

$\nu = 1226$ cm^{-1}. The effect of such overlapping, however, only shows up at relatively high concentrations of the impurities mentioned. The titanium oxychloride concentration of technical titanium tetrachloride does not usually exceed 0.2%, while that of thionyl chloride does not exceed 0.01%, and that of phosphorus oxychloride 0.005%; in such cases band overlapping does not show an appreciable effect on the determination of silicon tetrachloride content.

The sensitivity of determination is 0.02%. The error does not exceed 3-7% (relative).

The method developed has a number of advantages over chemical and emission spectrographic methods. They include: a shorter time for carrying out a determination; direct use of the titanium tetrachloride for analysis without preliminary hydrolysis; the possibility of designing apparatus for continuous determination of silicon in titanium tetrachloride; better reproducibility of the results.

The most important data obtained during development of techniques for determining these impurities in titanium tetrachloride by means of an IKS-12 spectrometer fitted with a NaCl prism, are given in the table.

SUMMARY

New impurities have been detected in titanium tetrachloride; they include thionyl chloride, phosphorus oxychloride, and carbon disulfide. Methods have been developed for the quantitative determinations of $SOCl_2$, $POCl_3$, CS_2, and $SiCl_4$ in titanium tetrachloride by infrared spectroscopy.

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SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN NIOBIUM

A. A. Baskin, E. I. Zazharov, K. I. Petrov, and E. I. Rzhekhina

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The main difficulty which arises during the spectrographic determination of impurities, in particular, iron, silicon, titanium, tantalum, and lead, in niobium metal is the preparation of reliable standards. Since niobium metal readily oxidizes in air at 600-700° it is expedient to prepare standards and samples in the form of niobium pentoxide. Published spectrographic methods only deal with the determination of tantalum and titanium [1, 7] and readily volatile lead, tin, cadmium, bismuth, and antimony [2] in niobium pentoxide. After the work described here had been completed a brief communication appeared on the use of the spectrographic method for the determination of a number of elements including iron, silicon, titanium, and tantalum [3] in niobium pentoxide. Unfortunately no information is given in this paper on the sensitivity and accuracy of the determination.

Choice of conditions. Results obtained. The most convenient light source for the spectrographic determination of impurities in powders at a high sensitivity level is a dc arc. Accordingly, during the simultaneous determination of iron, silicon, titanium, tantalum, and lead in niobium pentoxide, the spectra were excited in a dc arc. In order to prevent samples being thrown out of the electrode crater, the pentoxide was mixed beforehand with carbon powder (in the proportion of 2:1), while the current was kept at 6.5 amps for 15 sec during the initial period of arc burning, and was then raised for 12 amps. Excitation of the spectra at a low current, in addition, significantly increased the sensitivity and reproducibility of the determination of lead. The total exposure time was 2 min. Samples weighing 30 mg were placed in the carbon electrode crater which was 4 mm in diameter and 3mm deep. The lower electrode containing the sample served as the anode, while a carbon rod 6 mm in diameter was used as cathode. The spectra were photographed on a large Hilger quartz spectrograph using "diapositive" plates with a sensitivity of 0.25 GOST unit and "spectrographic type 1" with a sensitivity of 0.7 GOST unit. The spectrograph slit was illuminated with a one lens condenser.

The spectrum excitation conditions were chosen on the basis of study of the burning out curves obtained at arc current values of 10, 12, and 15 amps (at i = 12 amps in Fig. 1). Burning out curves for tantalum, titanium, silicon, and niobium on adding carbon powder to the sample, have, as a rule, two maxima each. We suggest that these maxima are determined by the formation of carbides during arc burning. It was established on the basis of the burning out curves that all the test impurities evaporated almost completely in 2 min when the current had values of 12 and 15 amps. However, for i = 15 amps there is observed a fairly intense background; it is better therefore to work at a current of 12 amps.

The internal standard method was adopted to improve the reproducibility of the determinations. Cobalt, which was added to standards and samples to a concentration of $8 \cdot 10^{-2}$ %, was used as an internal standard during silicon and iron determination. Niobium lines were used as reference lines for determination of titanium and tantalum. The analytical lines and the concentration ranges studied are given in Table 1. Typical calibration curves constructed within the coordinates $\log C - \Delta S$ are shown in Fig. 2.

Over the concentration ranges indicated, the curves are linear. By converting from blackening to intensity, iron, silicon, titanium, and lead can be determined with a sensitivity of $1 \cdot 10^{-3}$%, and tantalum with a sensitivity of $3 \cdot 10^{-2}$%.

The reproducibility of a single determination, which is characterized by the mean square error, amounts to 10% for tantalum and titanium, 11% for silicon, 13% for lead, and 16% for iron.

The reliability of the method was evaluated from the analytical results for samples to which known amounts of the test impurities had been added (Table 2). The figures given in the table testify to the completely satisfactory accuracy of the method developed.

Up to 1% of "third elements:" iron, silicon, lead, and calcium does not affect the sensitivity and accuracy of determination.

Preparation of spectrographically pure niobium pentoxide and preparation of standards. In order to obtain pure niobium pentoxide for preparing standards we have developed a method in which niobium is separated from tantalum on the basis of the difference in the extractability of their fluoride complexes with cyclohexanone [4-6].

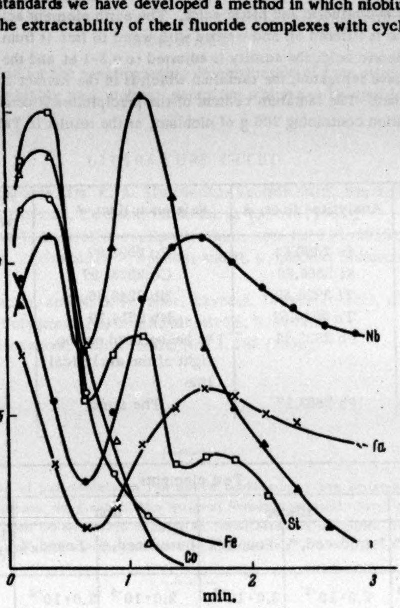

Fig. 1.

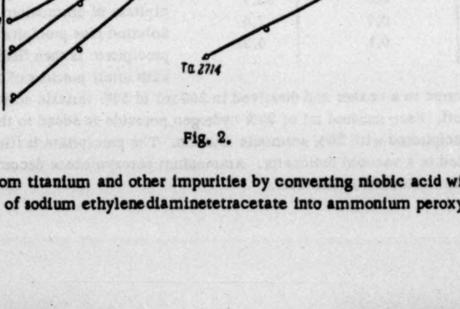

Fig. 2.

Niobium is separated from titanium and other impurities by converting niobic acid with hydrogen peroxide and ammonia in the presence of sodium ethylenediaminetetracetate into ammonium peroxyniobate $(NH_4)_3NbO_8$.

Under these conditions the impurities remain in solution. On heating, ammonium peroxyniobate readily changes into niobium pentoxide whose tantalum content is less than $1\cdot10^{-4}$%, while its titanium, iron, silicon, and lead contents do not exceed $1\cdot10^{-3}$%.

For preparing the fluoride solution, technical niobium, in the form of turnings, is placed in a platinum beaker and dissolved in a mixture of hydrofluoric and nitric acids. The earth element acids are precipitated from solution with ammonia, the precipitate is filtered off and washed with water to free it from nitrate ions. The precipitate is then dissolved in 40% hydrofluoric acid, the acidity is adjusted to 0.8-1 M and the tantalum extracted with cyclohexanone. After the phases have separated, the tantalum which is in the extract is precipitated with ammonia, filtered off, calcined, and weighed. The tantalum content of the precipitates is determined spectrographically. Tantalum is removed from a solution containing 200 g of niobium, as the results in Table 3 show, after four extractions.

TABLE 1

Test elements	Analytical lines, A	Reference lines, A	Test concentration range, %
Iron	Fe 2490.64	Co 2528.97	$3\cdot10^{-3}-1\cdot10^{-1}$
Silicon	Si 2506.89	Co 2528. 97	$3\cdot10^{-3}-1.10^{-1}$
Titanium	Ti 3234.52	Nb 3248.86	$3\cdot10^{-3}-3\cdot10^{-1}$
Tantalum	Ta 2714.67	Nb 2714.19	0.1 – 3.0
Lead	Pb 2833.07	The background on the right of the analytical line	$3\cdot10^{-3}-3\cdot10^{-2}$
	Pb 2663.17	The same	$3\cdot10^{-2}-3\cdot10^{-1}$

TABLE 2

Sample No.	Test elements									
	titanium		silicon		iron		tantalum		lead	
	Introduced, %	Found, %	Introduced, %	Found, %	Introduced, %	Found, %	Introduced,%	Found, %	Introduced, %	Found, %
1	$6.5\cdot10^{-3}$	$7.2\cdot10^{-3}$	$2.0\cdot10^{-3}$	$3.0\cdot10^{-3}$	$2.0\cdot10^{-3}$	$2.0\cdot10^{-3}$	–	–		
2	$2.0\cdot10^{-2}$	$1.8\cdot10^{-2}$	$6.0\cdot10^{-3}$	$5.0\cdot10^{-3}$	$6.5\cdot10^{-3}$	$6.3\cdot10^{-3}$	–	–	$6.5\cdot10^{-3}$	$6.5\cdot10^{-3}$
3	$6.5\cdot10^{-2}$	$6.6\cdot10^{-2}$	$2.0\cdot10^{-2}$	$2.0\cdot10^{-2}$	$2.0\cdot10^{-2}$	$2\ \cdot10^{-2}$	0.60	0.54	$5.0\cdot10^{-2}$	$4.0\cdot10^{-2}$
4	0.20	0.25	$6.5\cdot10^{-2}$	$7.2\cdot10^{-2}$	$6.5\cdot10^{-2}$	$6.6\cdot10^{-2}$	2.0	1.8	0.2	0.25

TABLE 3

Extraction	Amount of Nb and Ta in the extracts, mg	Ta content according to spectrographic analysis of the extracts, %	Amount of Ta extracted, mg
I	1820	35	637
II	1450	3.6	52.7
III	1000	0.7	7.0
IV	320	0.1	0.32

Niobium, which is contained in the aqueous phase, is precipitated with niobium, the precipitate is filtered off and washed with hot water. The precipitate which has been washed free of fluoride ions is transferred to a beaker, 100 ml of a 50% solution of ammonium ethylenediaminetetracetate and 250-300 ml of 25% ammonia solution are added, the mixture is cooled and 30% hydrogen peroxide added gradually with stirring until a coarse crystalline precipitate of ammonium peroxyniobate is formed. Solution plus precipitate are cooled for 1-2 hr, the precipitate is then filtered off and washed 2-3 times with small portions of 25% ammonia solution. The precipitate is again transferred to a beaker and dissolved in 200 ml of 50% tartaric acid heated to 50-70°, and the insoluble residue filtered off. Four-hundred ml of 30% hydrogen peroxide is added to the cooled solution and ammonium peroxyniobate precipitated with 25% ammonia solution. The precipitate is filtered off, washed with 25% ammonia solution, and dried in a vacuum desiccator. Ammonium peroxyniobate decomposes at 70-72° to form niobium pentoxide which is then calcined at 700-800°.

Standards are prepared on the basis of niobium pentoxide to which are added calculated amounts of tantalum, iron, silicon, titanium, and lead oxides, cobalt oxide being added as the internal standard. The mixture is placed in a platinum basin and ground for one hour. The remaining standards are prepared by diluting the original standard with the base and adding the internal standard.

SUMMARY

Methods have been developed for the spectrographic determination of iron, silicon, titanium, tantalum, and lead in niobium, and for obtaining highly pure niobium pentoxide which can be used for preparing spectrographic standards.

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DETERMINATION OF TITANIUM IN TITANIUM CARBIDE–NIOBIUM ALLOYS

E. E. Kotlyar and T. N. Nazarchuk

Institute of Metalloceramics and Special Alloys, Academy of Sciences,
Ukrainian SSR, Kiev

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Analysis of materials containing niobium, tantalum, and titanium is one of the most difficult problems in analytical chemistry. All known gravimetric methods involving the use of tannin, pyrogallol, acridine, 8-hydroxyquinoline etc. [1-5] require two, and in most cases, three reprecipitations which involves filtering and washing the precipitates. Not only are they tedious and inconvenient to carry out, but, as a number of studies have shown [6], they do not give sufficiently accurate results. The most promising approach would seem to be the direct titrimetric method of determining titanium in the presence of niobium, a method suggested by Winterstein [7], and also by Tomicek et al. [8]. In hydrochloric acid solutions titanium is reduced to its trivalent state by zinc amalgam in the presence of sodium fluoride. Under these conditions niobium is not reduced. According to Tomicek [8], in the presence of 25% tartaric acid, niobium is not reduced by zinc amalgam or amalgamated zinc. Under these conditions titanium is reduced to the trivalent state. Working with mercury presents certain difficulties. Accordingly, metallic cadmium and aluminum are widely used for reducing titanium.

The aim of the work described here was to obtain more accurate information on the reducibility of niobium and titanium by aluminum in the presence of masking agents, to establish the optimum conditions for reducing titanium, and to develop a method for determining titanium in TiC–Nb alloys.

EXPERIMENTAL

Metallic niobium was dissolved in a mixture of hydrofluoric acid with a few drops of concentrated nitric acid; sulfuric acid was then added and the liquid evaporated until SO_3 fumes were evolved. The sulfuric acid solution of niobium was diluted so that the niobium content of 10 ml of solution was not greater than 0.08-0.1 g. A titanium solution of the same concentration was prepared.

In order to study the effect of fluorides on the reduction of niobium in sulfuric-hydrochloric acid solutions by metallic aluminum, the following experiments were carried out. To solutions containing the same amount of niobium was added 20 ml of concentrated sulfuric acid and from 20 to 30 ml of concentrated hydrochloric acid. The volume of the solution was made up to 200 ml with water. Niobium was reduced with metallic aluminum in the presence of varying amounts of sodium or ammonium fluoride, the solution was cooled and the reduced solution titrated with a ferric alum solution in the presence of potassium thiocyanate. The results obtained are given in Table 1. Large amounts of fluorides (Table 1) are necessary to prevent reduction of niobium with metallic aluminum in sulfuric-hydrochloric acids.

It is more convenient to add ammonium fluoride, since it is appreciably more soluble than sodium fluoride; moreover, in the presence of ammonium fluoride sparingly soluble Na_3AlF_6 is not precipitated. The presence of varying amounts of hydrochloric acid in the mixture of sulfuric and hydrochloric acids has almost no effect on the reduction of titanium with metallic aluminum, at the same time, in the presence of hydrochloric acid the amount of niobium reduced increases sharply. Considerably smaller amounts of fluorides are required for preventing reduction of niobium in sulfuric-hydrochloric acid solutions than in hydrochloric acid solutions. Results on the reduction of niobium in sulfuric acid solutions in the presence of ammonium fluoride are given in Table 2. Accordingly, it is possible to prevent reduction of niobium by adding small amounts of ammonium fluoride. The following results were obtained (Table 3) during titration of mixtures of niobium and titanium in a sulfuric acid medium in the presence of ammonium fluoride.

When even small amounts of hydrochloric acid (about 5 ml) are added to sulfuric acid solutions of niobium and titanium salts in the presence of ammonium fluoride, appreciable reduction of niobium occurs. Not only fluorides, but also tartaric, oxalic, and citric acids, and sodium ethylenediaminetetracetate (Table 4) can be used for complexing niobium into a complex which is not reduced by metallic aluminum. On the basis of the results given in Table 4, one can conclude that quadrivalent titanium, in the presence of fluorides, oxalic, citric, and tartaric acids, and sodium ethylenediaminetetracetate can be readily reduced with metallic aluminum to the trivalent state, while quinquevalent niobium is not reduced under these conditions.

TABLE 1. Effect of Fluorides on Reduction of Quinquevalent Niobium with Aluminum in Sulfuric-Hydrochloric Acid Solutions (Niobium taken 0.044 g)

NaF, added, g	Extent to which niobium is reduced	Color of the niobium solution	NH_4F added, g	Extent of reduction	Color of the niobium solution
–	3.7	Black	–	3.7	Black
2	4.2	Brown	2	3.8	Brown
3	4.4	Ditto	6	4.5	Ditto
5	4.7	Yellow	10	4.9	Bright-yellow
7.5	4.8	Bright-yellow	12	4.97	Colorless
10	4.93	Almost colorless	15	4.98	Colorless
15	4.94	Ditto			

TABLE 2. Effect of Fluorides on the Reduction of Niobium in a Sulfuric Acid Medium (0.044 g niobium taken)

NH_4F, added g	Extent to which niobium is reduced
0.2	4.65
0.4	4.88
0.6	5.00
1.0	5.00

TABLE 3. Determination of 0.0884 g of Titanium in a Sulfuric Acid Medium in the Presence of Niobium

Niobium added, g	Ti: Nb ratio	NH_4 added, g	Found, g
0.096	1:1	0.5	0.0886
0.096	1:1	1.0	0.0886
0.144	1:1.5	1.0	0.0887
0.198	1:2	1.5	0.0886

EXPERIMENTAL

0.1-0.2 g of a TiC–Nb alloy is dissolved in 10-15 ml of a HF + HNO_3 mixture. When dissolution is complete the solution is evaporated to a small volume, 10 ml of sulfuric acid is added and the liquid evaporated to the appearance of white SO_3 fumes. After being cooled, the solution is transferred to a 250 ml conical flask; 20-25 ml of concentrated sulfuric acid is added, followed by 1 g of ammonium fluoride or 5-7 g of citric or tartaric acid, the solution is diluted to 100 ml with water and 1.5-2.0 g of metallic aluminum added in individual portions while the solution is continuously cooled. When turbulent liberation of hydrogen in the cold is complete, a stopper with two inlet tubes is fitted into the flask; one is connected to a CO_2 supply while the other serves for leading off the gas. The flask is placed on a hotplate and is boiled until the aluminum has dissolved completely; the solution is then cooled while the CO_2 is passed through it and is rapidly titrated with a ferric alum solution until it has a rose color. The ferric alum solution is standardized against a standard solution of titanium or ferrotitanium.

Should the alloy not dissolved in the HF + HNO_3 mixture, it is fused in a platinum crucible with potassium pyrosulfate. The melt is leached into 20 ml of 30% tartaric or citric acid, the solution is transferred into a conical flask and 20 ml of concentrated sulfuric acid added; the procedure outlined above is then followed.

Titanium carbide alloys containing different amounts of niobium were analyzed by the method suggested using citric acid. Results of parallel determinations are given below:

Sample		Titanium found	
1	3.52	3.44	3.48
2	14.50	14.40	14.42

Sample	Titanium found		
3	28.70	28.82	28.74
4	58.67	58.60	58.67
5	69.55	69.70	69.60

TABLE 4. Effect of Masking Agents on the Reduction of Titanium and Niobium in Sulfuric Acid Solutions by Metallic Aluminum (total volume of solution 200 ml)

Concentrated		Added, g				ml of 0.078 N $NH_4Fe(SO_4)_2$ solution used
H_2SO_4, ml	HCl, ml	citric acid	tartaric acid	oxalic acid	sodium ethylenediaminetetracetate	
			0.088 g titanium taken			
20	—	—	—	—	—	23,30
20	—	2,5	—	—	—	23,35
20	—	5,0	—	—	—	23,30
20	—	7,5	—	—	—	23,25
20	—	10,0	—	—	—	23,35
20	—	—	3,5	—	—	23,4
20	—	—	7,0	—	—	23,35
20	—	—	10,0	—	—	23,30
20	—	—	—	2,0	—	23,35
20	—	—	—	4,0	—	23,30
20	—	—	—	6,0	—	23,35
20	—	—	—	—	5,0	23,40
20	—	—	—	—	10,0	23,45
			0.096 g niobium taken			
20	—	—	2,0	—	—	0,6
20	—	—	3,5	—	—	0,3
20	—	—	7,0	—	—	0,0
10	10	—	7,0	—	—	2,1
20	—	2,5	—	—	—	0,2
20	—	5,0	—	—	—	0,0
10	10	5,0	—	—	—	1,5
20	—	—	—	2,0	—	0,2
20	—	—	—	4,0	—	0,0
20	—	—	—	—	5,0	0,0
20	—	—	—	—	10,0	0,0

SUMMARY

A method has been developed for the titrimetric determination of titanium in titanium–niobium alloys after its reduction with metallic aluminum in the presence of fluorides, oxalic, tartaric, and citric acids or sodium ethylenediaminetetracetate in a sulfuric acid medium. Hydrochloric acid promotes reduction of niobium. The method has been used for the determination of titanium in alloys of titanium carbide and metallic niobium.

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ELEMENTAL-ORGANIC ANALYSIS BY THE "WET COMBUSTION" METHOD

COMMUNICATION 4. DETERMINATION OF CARBON, SILICON, AND ALUMINUM IN POLYMERIC ORGANOALUMINOSILOXANES*

A. P. Terent'ev, B. M. Luskina, and S. V. Syavtsillo**

M. V. Lomonosov Moscow State University

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Existing methods for the analysis of silicoorganic materials which are based on combustion in an oxygen stream, permit determination of carbon, hydrogen, and silicon [2-3], or carbon, hydrogen, silicon, and halogen (or sulfur) [4] on one aliquot. For the analysis of silicoorganic compounds containing metal atoms, however, these methods are not suitable for the determination of both silicon and metal. It is best to use the "wet combustion" method in such cases [5].

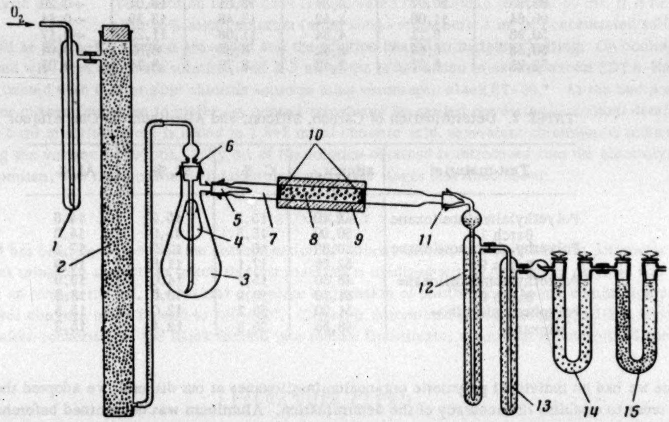

Fig. 1. Wet combustion apparatus. 1) Bubble counter filled with concentrated sulfuric acid; 2) askarite column for purifying the oxygen; 3) reaction flask; 4) side tube, fused into the flask, for introducing chromic acid; 5) ground joint; 6) ground stopper with tube for introducing oxygen; 7) quartz tube (200 ml long, 8-10 mm diameter); 8) catalyst—chromic oxide on pumice; 9) electric oven at 700-750°; 10) loose fitting asbestos plugs; 1)) ground joint; 12) halogen absorber containing pieces of glass rod moistened with an acetic acid solution of hydrazine (pH 6); 13) flask containing pieces of glass rod moistened with concentrated sulfuric acid; 14) tube containing anhydrone; 15) tube containing askarite and anhydrone.

Wet combustion, as a method of breaking down silicoorganic compounds which contain various metals and metalloids, can be used in a very wide variety of cases, since in addition to carbon and silicon, it also permits determination of other elements which remain in the filtrate after removal of the carbon and silicon. Complete oxidation of various polymers is possible by choosing appropriate oxidizing mixtures and decomposition conditions.

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* For communication 3, see [1].

** L. N. Karabashkina took part in the experimental work.

Earlier [6], we suggested a method for oxidizing silicoorganic compounds with sulfuric and chromic acids in an oxygen stream for the determination of carbon and silicon, and carbon, nitrogen, and copper or iron in organic compounds containing metals. It was established in the course of the work described in the present article that it is necessary, in order to destroy polymeric organoaluminosiloxanes by the wet combustion method, to heat the test material in concentrated sulfuric acid beforehand. It was obvious that during such treatment the bond $\equiv\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Al}}=$ [7] was broken, and further oxidation of these siloxanes with chromic acid proceeded appreciably more rapidly. The silica formed during this stage was removed from the sulfuric acid by filtration, gelatin solution being added to accelerate filtration. The silicon was then converted into sodium fluorosilicate and determined titrimetrically [8]. Aluminum was determined in the filtrate after removal of silicon. In order to separate aluminum from chromium which is always contained in appreciable amounts in the sulfuric acid solution after combustion, we adopted electrolysis with a mercury cathode [9]. Chromium was thereby held by the mercury, while the aluminum remained in solution. Aluminum was determined titrimetrically with sodium ethylenediaminetetracetate (EDTA-Na) [10]. Carbon was determined gravimetrically as usual.

TABLE 1. Determination of Aluminum

Aliquot of polyphenyl-aluminosiloxane, mg	Al, mg				
	content of the aliquot	added	total amount	found	difference
89,95	10,97	4,84	15,81	16,01	+0,20
90,64	11,06	2,42	13,48	13,59	+0,11
50,98	6,22	4,84	11,06	11,23	+0,17
50,53	6,14	2,42	8,56	8,52	—0,04
52,25	6,37	2,42	8,79	8,74	—0,05

TABLE 2. Determination of Carbon, Silicon, and Aluminum on One Aliquot

Test material	aliquot, mg	C, %	Si, %	Al, %
Polyethylaluminosiloxane Batch 1	49,10	15,3	15,2	14,6
	50,90	15,5	15,0	14,3
Polyethylaluminosiloxane Batch 9	50,88	16,7	12,2	17,2
	52.58	17,1	11,8	16,9
Polyethylauminosiloxane Batch 21	48,30	15,1	14,0	13,9
	51,70	14,9	13,6	13,8
Polyphenylalumino-siloxane	51,20	35,7	12,0	15,5
	48,55	35,3	12,4	15,3

Since we had no individual polymeric organoaluminosiloxanes at our disposal, we adopted the following procedure in order to establish the accuracy of the determination. Aluminum was determined beforehand by the suggested method (12.2% Al) in technical polyphenylaluminosiloxane. Next, a known volume of aluminum sulfate solution prepared from aluminum metal Mark AB1 was introduced into the reaction flask 3 (Fig. 1), and the liquid evaporated almost to dryness, an aliquot of the siloxane with the known aluminum content was introduced, and oxidation and determination of aluminum carried out as described below. The results obtained are given in Table 1.

The carbon, silicon, and aluminum contents of samples of technical polymeric ethyl- and phenylaluminosiloxanes were determined on one aliquot by the suggested method. It is clear from the results obtained that there is satisfactory agreement between parallel determinations.

EXPERIMENTAL

Into a dry reaction flask 3 (Fig. 1) containing an aliquot of test material is introduced 5 ml of concentrated sulfuric acid,* while through side tube 4 is introduced 1.5-2 ml of chromic acid.** The flask is connected, as shown in Fig. 1, oxygen is passed through for 2-3 min and weighing tube 15 connected. Without stopping the oxygen flow, the flask is immersed for 10-15 min in a bath heated to 150-160°, and on cooling a small amount of chromic acid is added from side tube 4; liberation of carbon dioxide bubbles is observed during this stage. Oxidation usually proceeds quietly without foaming. When any visible reaction has stopped the flask is again heated at the same temperature for 30 min.

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* The sulfuric acid is heated beforehand for 40-50 min in order to destroy any possible organic impurities, and then cooled in a flask fitted with a ground glass calcium chloride tube.

** Seventy g of chromium trioxide is dissolved in 100 ml of water and boiled for 3-5 min. The cooled solution is filtered through a glass filter.

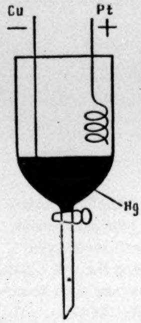

Fig. 2. Electrolytic cell.

The carbon content is determined from the increase in weight of tube 15 filled with askarite following from the absorption of carbon dioxide. Silicon and aluminum are determined in the contents left in reaction flask 3 after combustion. For this purpose the flask is disconnected, the silica adhering to the walls is washed off with water and then filtered off, the silicon is finally determined titrimetrically by a method described earlier [8].

Aluminum is determined as follows. After removal of the silicon, the sexivalent chromium in the filtrate is reduced by heating with a few drops of methanol. The solution is transferred into a 200 ml standard flask, an aliquot of this solution (50 ml) is transferred into an electrolytic cell (Fig. 2) containing 30-40 ml of mercury metal and 50-60 ml of water. The electrodes are connected to a dc current source and electrolysis carried out with a current of 5 amps at a voltage of 22 v over a period of 100-120 min. The colorless solution obtained in syphoned from the electrolytic cell into a conical flask, and the electrolytic cell washed 4-5 times with 5-7 ml lots of water. The solution in the flask is evaporated to a volume of about 50 ml, it is neutralized with 25% alkali solution (using congo red paper), 1 ml of concentrated sulfuric acid and 20 ml of 0.01 M EDTA-Na solution are added and the solution heated to incipient boiling. On cooling, the solution is neutralized with 1 M ammonia solution, and 2-3 ml of the latter added in excess; excess EDTA-Na solution is then rapidly titrated with 0.01 M zinc chloride solution using chromogen black ET-00.* At the end point there is a distinct color change from blue to violet. A control test should be carried out during aluminum determination. For this purpose 5 ml of sulfuric acid is added to 1.5-2 ml of chromic acid, sexivalent chromium is reduced and water is added to bring the volume to 200 ml. Fifty ml of the solution obtained is introduced into the electrolytic cell to remove the chromium, and the solution then taken through all the stages described above.

SUMMARY

A method has been developed for the determination of carbon, silicon, and aluminum in polymeric organoaluminosiloxanes using one aliquot, in which the test material is oxidized with a mixture of chromic and sulfuric acids at 150° in an oxygen stream. Additional complete combustion of possible incomplete combustion products is carried out over chromic oxide heated to 700-750°. Carbon is determined gravimetrically; silicon is determined titrimetrically after conversion of the silica formed into sodium fluosilicate; aluminum is determined complexometrically.

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*100 mg of indicator is carefully mixed with 10 mg of finely ground sodium chloride [10]; this mixture is added on the tip of a microspatula.

DETERMINATION OF FURANE AND TETRAHYDROFURANE COMPOUNDS BY INFRARED SPECTROSCOPY

N. I. Shuikin, B. V. Lopatin, and B. L. Lebedev

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow

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Increasing attention has been given in recent years to the chemistry of furane compounds, including problems relating to catalytic hydrogenation, hydrogenolysis, and alkylation of oxygen-containing heterocyclic compounds. These problems cannot be solved, however, without a well established analytical background. Until recently no methods have been published on the determination of furane compounds containing alkyl radicals in the side chain. We have successfully used gas liquid chromatography for determination of furane, tetrahydrofurane and their homologs [1].

In the work described here an attempt was made to use infrared spectroscopy for determination of furane and tetrahydrofurane compounds. There is already a well developed technique for the determination of methyl and methylene groups on the basis of the intensity of the respective absorption bands in the infrared, in the case of alkanes of normal and branched structure and also for cyclanes [2-5]. A considerably smaller amount of work has been devoted to studies of the structure of the alkyl radical in aromatic and unsaturated compounds, and in organic acids etc. [6-8]. It has been shown in these papers that the intensity of the absorption bands of CH_2- and CH_3- groups in the infrared spectrum is not proportional to the number of the respective groups, and that methods used for determination of alkanes should be developed further so that they can be applied for determination of compounds in the classes indicated above.

The work described here is devoted to a study of the possibility of using the method developed for alkenes to the determination of the number of methyl and methylene groups in the alkyl radicals of furane and tetrahydrofurane compounds.

Taking into account the advantages and disadvantages of the various methods, we settled on Jones' method [4] which permits the number of CH_2- and CH_3- groups to be determined reasonably accurately and most rapidly on the basis of infrared spectra.

We obtained the infrared absorption spectrum in the region 2800-3100 cm^{-1} for each representative of both the furane and tetrahydrofurane series on a double beam UR-10 infrared spectrophotometer. The compounds were examined in CCl_4 solution at a concentration of 0.1-0.03M in constant path length cells. The path lengths were 1.05 0.25 mμ. The spectral slit width was 2.5 cm^{-1}. At this slit width the error introduced into the measurement of the value of peak intensity as a result of the terminal slit width, was insignificant, and as calculations made by Ramsey's method showed, decreased the value of the intensity by less than 20%. At the concentrations we used the solutions conform well to Beer's law. Calculations were made using the formula:

$$I = D_{max}/Cd$$

where D_{max} is the optical density at maximum absorption; C is the concentration of the test material, M; $\underline{d}$ is the path length, cm; I is the intensity, which is proportional to the absorption coefficient. For analytical purposes we used the absorption bands of the asymetrical vibration of the CH_2- groups and the double degenerated vibrations of the CH_3- groups. The relation of the bands in the infrared spectra was established according to the data in the paper by Shappard and Simpson [9], which has been confirmed in subsequent articles [2-4, 10, 11]. Since the absorption bands of CH_2- and CH_3- groups partially overlap, in a small number of cases the complex contour of the absorption bands was resolved into its components; this was made considerably easier by the fact that the absorption bands had a contour which was symmetrical and comparatively well described by dispersion formulas.

Table 1 contains the absorption band frequencies of the antisymmetric vibration of the CH_2-group and the twice degenerated vibration of the CH_3-group for standard compounds of the furane and tetrahydrofurane series. All the compounds used as standards were carefully purified by distillation in a high efficiency fractional distillation column. The purity of the preparations were checked by gas liquid chromatography. Their constants are given in Table 2. The position of the absorption bands of the methyl and methylene groups for all the compounds, apart from α-methylfurane and α-ethylfurane, corresponds to collected published data 2962 ± 10 cm^{-1} and 2926 ± 10 cm^{-1} [12].

TABLE 1. Position of the Absorption Bands of the Antisymmetric Vibration of the Methylene Group and of the Twice Degenerated Vibration of the Methyl Group

Compound	Absorption band frequency, cm^{-1}		Compound	Absorption band frequency, cm^{-1}	
α-Methylfurane	2956	2926	α-n-Propyltetrahydrofurane	2964	2934
α-Ethylfurane	2985	2940	α-Isobutyltetrahydrofurane	2962	2931
α-n-Propylfurane	2964	2935	α-Propyl-β-ethyltetrahydrofurane	2964	2934
α-n-Butylfurane	2961	2933	α-Ethyl-α'-propyltetrahydrofurane	2965	2934
α-n-Amylfurane	2960	2932	α-Methyl-α'-propyltetrahydrofurane	2966	2933
α-Methyltetrahydrofurane	2974	–		CH_3	CH_3
α-Ethyltetrahydrofurane	2967	2937			

TABLE 2. Physicochemical Properties of Standard Compounds

Compound	t° b. p.°/mm	d^{20}_4	$n^{20}D$
α-Methylfurane	63-64	0.3188	1.4340
α-Ethylfurane	92-93	0.9020	1.4415
α-n-Propylfurane	114-115	0.8308	1.4400
α-n-Butylfurane	137-138	–	1.4460
α-n-Amylfurane	163-164	–	1.4472
α-Methyltetrahydrofurane	78-79	0.8563	1.4070
α-Ethyltetrahydrofurane	107-107	0.8550	1.4160
α-n-Propyltetrahydrofurane	132-133	0.8562	1.4226
α-Isobutyltetrahydrofurane	149-150	0.8485	1.4262
α-Propyl-β-ethyltetrahydrofurane	68-70 [13]	0.8558	1.4380
α-Methyl-α'-propyltetrahydrofurane	144-145 [5]	0.8507	1.4240
α-Ethyl-α'-propyltetrahydrofurane	90-92 [63]	0.8516	1.4295

An appreciable shift in the position of the absorption bands was only observed in the case of α-ethylfurane and -methylfurane, while splitting of the absorption band into its components was also a characteristic feature of α-methylfurane. These effects are determined, presumably, by strong interaction between the groups near to the ring and the furane ring.

The intensity of the absorption bands of the CH_2- and CH_3-groups in the standard compounds is given in Table 3; the information is taken from the paper by West et al. [13].

The intensity of the CH_2-groups in the ring is excluded from the total intensity of the absorption bands of the methylene group in the case of compounds of the tetrahydrofurane series. According to our measurements carried out for tetrahydrofurane, ΣI_{CH_2} = 110 units, i.e., converted to one CH_2-group 27 units. This value is significantly lower than that for cyclanes; e.g., according to published results [2] the intensity of the absorption band of the CH_2-groups in cyclohexane is 89 units calculated in terms of one group.

The intensity of the absorption bands of the methyl and methylene groups is additively dependent on the number of the respective groups both for the furane and tetrahydrofurane series (Table 3).

TABLE 3. Intensities of the Absorption Bands of Methyl and Methylene Groups in Standard Compounds ($I_{CH_3[CH_2]} = \Sigma I_{CH_3[CH_2]}/n$, where n is the number of CH_3 or CH_2 groups; ΔI is the difference between the value and the intensity, relating to one group of the corresponding band in alkanes)

Compound	ΣI_{CH_3}	I_{CH_3}	ΔI	ΣI_{CH_2}	I_{CH_2}	ΔI
α-Methylfurane	24.37	61	–	–	–	–
α-Ethylfurane	69	69	81	36	36	39
α-n-Propylfurane	139	139	11	87	43	32
α-n-Butylfurane	123	123	27	111	37	38
α-n-Amylfurane	142	142	8	195	49	26
α-Methyltetrahydrofurane	90	90	60	–	–	–
α-Ethyltetrahydrofurane	120	120	30	46	46	29
α-n-Propyltetrahydrofurane	150	150	0	142	71	4
α-Isobutyltetrahydrofurane	223	112	–	54	54	21
α-Propyl-β-ethyltetrahydrofurane	290	145	–	170	63	–
α-Ethyl-α'-propyltetrahydrofurane	249	124	–	110	56	–
α-Methyl-α'-propyltetrahydrofurane	234	117	–	140	70	–
n-Alkanes according to [12]	–	150	0	–	75	0

An appreciable drop in intensity, as compared with alkanes, is only observed in the first groups nearest to the furane ring. The effect of the tetrahydrofurane ring is significantly weaker.

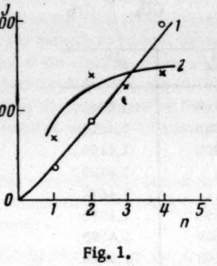

Fig. 1.

With further increases in the chain of the alkyl radical the intensity of the absorption bands of the CH_2- and CH_3-groups approximates to the intensity of the corresponding groups in n-alkanes.

Figure 1 shows the relation between the total intensity of the absorption bands of the CH_2-groups in a series of furane compounds and their number (curve 1), and the increases in the intensity of the absorption band of the CH_3-group as its distance from the ring increases for the same compounds (curve 2). The deviation from the corresponding curves observed in some cases can, presumably, be explained by the inaccuracy in resolution of the bands. It should be pointed out that in the case of the tetrahydrofurane series, the effect of the ring on the substituent in the β-position is hardly observable even for groups near the ring. Thus in the case of short alkyl radical having one or two carbon atoms, it is possible to distinguish the position of the alkyl radicals in the tetrahydrofurane ring.

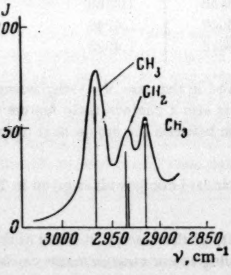

Fig. 2.

We used the results obtained during studies of standard compounds for determining a number of materials obtained during the alkylation of furane and tetrahydrofurane. Thus, in particular, we established the structure of products later identified as α-methyl-α'-ethylfurane, triethyltetrahydrofurane, and isobutyltetrahydrofurane. The results are given in Table 4. This table includes the intensity of the absorption bands of the CH_2- and CH_3-groups (ΣI_{CH_2}, ΣI_{CH_3}), the number of methyl and methylene groups found n_{CH_3} and n_{CH_2}, and the error in determining the number of groups Δ_n.

Since the spectrum of α-methyl-α'-ethylfurane exhibits a characteristic splitting of the absorption bands of the methyl group, and a shift in the band of the CH_2-group (see Fig. 2) it was possible to establish the type of substitution for this compound.

Results obtained by infrared spectroscopy were confirmed by other physicochemical methods. Thus by introducing the necessary correction, and increasing the intensity of the band to a value found during studies of standard samples, thereby taking into account the drop in intensity for the groups nearest to the ring, methods which have been developed for the alkanes can be successfully applied to the determination of the number of CH_2- and CH_3-groups in furane and tetrahydrofurane compounds.

TABLE 4. Analytical Results for Some Products Obtained during the Alkylation of Furane and Tetrahydrofurane

Compound	ΣI_{CH_3}	ΣI_{CH_2}	n_{CH_3}	n_{CH_2}	Δn_{CH_3}	Δn_{CH_2}
α-Methyl-α'-ethylfurane	56—CH_3 74—C_2H_5	32	1,5 1,1	0,9	0,5 0,1	0,1
Triethyltetrahydrofurane	354	147	2.7	3,2	0,3	0,2
Isobutyltetrahydrofurane	235	54	2.0	1,0	0	0

Notes: 1) The band of the CH_3-group splits into its components. 2) The intensity which is determined by the methylene groups in the tetrahydrofurane ring is excluded from the total intensity of the CH_2-groups.

SUMMARY

It has been shown that it is possible to use the methods for determining alkanes for the determination of the number of methyl and methylene groups in the alkyl radicals in compounds of the furane and tetrahydrofurane series.

The additive character of the relation between the intensity of the absorption bands of CH_2- and CH_3-groups in the infrared spectrum and the number of the corresponding groups has been demonstrated.

The relation between the position and intensity of the absorption bands of CH_2- and CH_3-groups and the position of these groups with respect to the furane and tetrahydrofurane ring has been examined.

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DETERMINATION OF ALIPHATIC ACID HYDRAZIDES BY POTENTIOMETRIC TITRATION WITH SODIUM NITRITE

A. P. Grekov and M. S. Marakhova

All-Union Scientific-Research Institute of Chemical Reagents, Khar'kov Branch

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A number of methods are known at present for the quantitative determination of aliphatic acid hydrazides [1-4]. We have extended an analytical method for the determination of acid hydrazides by potentiometric titration with sodium nitrite which was suggested earlier for aromatic acid hydrazides [5] to cover the hydrazides of aliphatic acids. The basis of this method is the fact that aliphatic hydrazides also react readily with nitrous acid in a hydrochloric acid medium according to the equation:

$$RCONHNH_2 + HNO_2 \longrightarrow RCON_3 + 2H_2O$$

Aliphatic hydrazides, in contrast to aromatic hydrazides, quantitatively react with nitrous acid only at a strictly defined acidity. This is explained by the fact that in the presence of a large excess of aqueous solutions of mineral acids aliphatic hydrazides hydrolyze to hydrazine and the corresponding acid according to the scheme [1]:

$$RCONHNH_2 \xrightarrow{HOH} RCOOH + N_2H_4$$

Since a molecule of hydrazine interacts with two molecules of nitrous acid according to the equation [6]:

$$N_2H_4 + 2HNO_2 \rightarrow N_2 + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

high results are obtained for such hydrazides.

As the reactivity of the hydrazides decreases the accuracy with which they can be determined decreases. Thus the hydrazides of formic and methoxyacetic acid were determined with an error of up to 10%. On the other hand, the introduction of a phenyl ring into the α-position of aliphatic hydrazides renders such compounds less sensitive to the effect of mineral acids. Like the hydrazides of aryl carboxylic acids they are readily determined over a wide acidity range.

EXPERIMENTAL

The hydrazides of acetic, propionic, butyric, phenylacetic, phenoxyacetic, formic, and methoxyacetic acids were carefully purified; the content of the given preparation in a test sample was about 100%.

The experimental technique was similar to that described previously [7-9]. All experiments were carried out at room temperature. A 0.01 N sodium nitrite solution was used as the titrant, it was standardized potentiometrically against sulfanilic acid [7]. 0.05 M solutions of the hydrazides were prepared by dissolving accurately weighed aliquots in benzene. Hydrochloric acid and KBr were added to 10 ml of the hydrazide solution, titration was then carried out from a 10 ml microburet with 0.02 ml scale divisions, the drawn out tip of this buret being immersed in the solution being titrated. At the beginning of titration the potential was established almost instantaneously; near the end point the potential was established after 50-10 min. Addition of KBr improves the inflection in the potential.

The effect of hydrochloric acid concentration on the accuracy of determination of alkyl hydrazides is evident from the results given in Table 1. The best results are obtained in a medium of 0.03-0.05 M HCl. Results of the determination of aliphatic acid hydrazides are given in Table 2.

The mean result of not less than five determinations is given in the last column. Statistical treatment of the results [10] shows that the experimental accuracy is not less than 1%. The total nitrogen content of all the test hydrazides as determined by the Dumas method confirmed the correctness of the results of the titrimetric method.

TABLE 1. Effect of Hydrochloric Acid Concentration on the Results of Titrating Acetyl Hydrazide with Sodium Nitrite

C_{HCl}, M	Found, %	C_{HCl}, M	Found, %
0,01	106,0	0,30	106,2
0,02	104,9	0,60	110,6
0,03	100,2	1,25	130,1
0,05	100,8	2,50	151,8
0,10	102,8	5,00	193,0
0,15	106,2		

TABLE 2. Determination of Some Hydrazides

Acid hydrazides	Sample wt., mg	Found, %
Acetic	3,70	100,2
Propionic	4,40	99,7
Butyric	5,11	100,4
Phenylacetic	7,51	100,3
Phenoxyacetic	8,31	100,4

The method can also be carried out by a macro variant, the amounts of the reagents being appropriately increased.

EXPERIMENTAL

An aliquot of hydrazide (0.01-0.05 mM) is dissolved in 5-10 ml of benzene in a 50-100 ml beaker; 10 ml of 0.05 N hydrochloric acid and 0.1-0.2 g potassium bromide are added, and a platinum electrode (a quinhydrone or saturated calomel electrode is used as the auxiliary electrode) immersed in the solution.

While the solution is vigorously stirred with a mechanical stirrer 0.01 N sodium nitrite solution is added in definite portions from a microburet (the tip of which is immersed in the liquid). The end point is established on the basis of the maximum $\Delta E/\Delta V$.

SUMMARY

A method has been developed for the quantitative determination of aliphatic acid hydrazides by potentiometric titration with sodium nitrite. It has been shown that aliphatic hydrazides are readily determined (with an error of up to 1%) in a medium of 0.03-0.05 M HCl.

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A COLORIMETRIC METHOD OF DETERMINING PROLINE

M. A. Torban and V. I. Smyshlyaeva

Stavropol Scientific Research Institute of Vaccines and Serums

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Several methods are known for the photometric determination of proline. The most widely used of these methods is that of Guest [1]. Nevertheless, apart from the difficulties involved, current methods give inaccurate results. Accordingly, we set ourselves the problem of developing an improved photometric method of determining proline.

The method developed is based on the fact that the reaction product of proline with ninhydrin is readily extracted with isobutanol to give a bright-red colored solution.

The following procedure is adopted for determination of proline in protein hydrolyzates: 1 ml of test protein is hydrolyzed in a boiling water bath for 15 hr with an equal volumeof 4 N hydrochloric acid. The hydrolyzate is then evaporated to dryness to remove most of the hydrochloric acid. Four ml of 3% trichloroacetic acid and 1 ml of 10% phosphomolybdic acid solution are added to the dry residue. The trichloroacetic acid and phosphomolybdic acid are added to remove unhydrolyzed protein and peptones. The residue is filtered off. To 0.5 ml of the filtrate is added 0.5 ml of a 2% aqueous solution of ninhydrin. The mixture is placed for 10 min in a boiling water bath and 50 ml of water are then added.

When hydrochloric acid is present at a concentration higher than 0.1 N a violet color does not appear on boiling the protein hydrolyzate with ninhydrin. But on dropping the concentration only a little further to 0.062 N the color with ninhydrin develops completely; accordingly, a one stage evaporation of hydrochloric acid from the hydrolyzate is sufficient for realizing the color reaction. However, when the hydrolyzates contain traces of hydrochloric acid, the isobutanol extract has a violet not a red color. A relatively large amount of water – 50 ml – is added to the hydrolyzate to destroy the violet tinge, and when this is done the isobutanol acquires a red color.

After adding water to the colored solution, 10 ml of isobutanol is added and the whole carefully shaken for 3 min. After the layers have separated, the upper, alcoholic layer has a bright rose color.

The result obtained is multiplied by 0.5 during calculation of the proline content of the protein hydrolyzates.

Experiment showed that the best results are obtained on working with hydrolyzates containing 80-2000 mg % of proline. The limiting sensitivity of the reaction is 15 mg% proline.

In model experiments with amino acids dissolved in mixtures of trichloroacetic acid and phosphomolybdic acid, it was found that the color of the isobutanol layer is specific for proline and is not observed in the case of solutions of other amino acids: histidine, lysine, tyrosine, tryptophane, phenylalanine, cystine, cysteine, serine, leucine, alanine, glycine, norleucine, glutamic and aspartic acids, and also urea.

The error does not exceed ± 4% in parallel determinations of various amounts of proline in pure solutions. On adding proline to protein hydrolyzates the error rises to ± 12%. The method gives more accurate results than Guest's method (the error in the latter amounts to ± 19%). During precipitation of native protein with phosphomolybdic acid the precipitate entrains some of the phosphomolybdate from solution. Nevertheless, varying final concentrations of phosphomolybdic acid (from 1 to 2.5%) do not affect the color sensitivity.

Formaldehyde (at a final concentration of 1-10%), sulfosalicylic and trichloroacetic acids (at a final concentration of 0.6-0.9%), and ethanol and acetone at concentrations up to 6% do not interfere with proline determination.

The red colored solutions do not conform to Beer's law so that a calibration curve must be used.

The optical density should be measured with a light filter having maximum transmission at 533 mμ for photometric determination of proline.

Boiling proline with 18% hydrochloric acid for 12 hr does not lower the intensity of the color subsequently obtained. Accordingly, hydrolysis does not destroy proline. Alkaline hydrolysis of protein leads to partial destruction of proline. On boiling proline solutions with 0.5 N sodium hydroxide for 12 hr the proline content decreases by 32%.

Proline could not be detected in nonhydrolyzed 10% solutions of casein, gelatin, and crystalline ovoalbumen. Only traces of proline could be detected in the same proteins after they had been subjected to the action of 1% pepsin for 2 hr at 24° in the presence of 1% hydrochloric acid.

TABLE 1. Proline Content of Protein Hydrolyzates as a Percentage of Total Resin taken as 100%

Protein	Proline content, %	
	found	published data
Ovoalbumen	5.1	4-5 [2, p. 368]
Casein	7.5	8, 2 [2, p. 371]
Gelatin	20.5	–
Serum protein	8.0	–

TABLE 2. Determination of Proline in Aqueous Solutions

Proline concentration, mg	Proline found, mg	
	without hydrochloric acid	in the presence of 0.062 N hydrochloric acid
5	5.3	10.6
4	4.0	8.0
3	2.9	5.8
2	2.1	4.2
1	0.9	1.8

Proteins and peptides containing proline do not give a color reaction for this amino acid before hydrolysis. Results of the determination of proline in acid hydrolyzates of 10% solutions of ovoalbumen, casein, gelatin, and also in hydrolyzates of 30 horse antidiptheria sera are given in Table 1.

On adding 5 mg of proline to 1 ml of a protein solution subjected to hydrolysis, all the proline was determined; 10.2% of proline was found in ovoalbumen, 12.4% in casein, and 25.5% in gelatin.

When the proteins to which proline was added were not subjected to hydrolysis, determination of proline was impossible since the nonhydrolyzed proteins were precipitated with phosphomolybdic acid and entrained large amounts of proline. Thus, when the final concentration of casein was 0.6%, it entrained 11% of the proline, while ovoalbumen and gelatin at the same concentrations entrained 54% and 59%, respectively. Complete acid hydrolysis of protein is essential for quantitative determination of proline.

Table 2 contains results of experiments with aqueous solutions of proline with and without hydrochloric acid; the final HCl concentration was 0.062 N.

Table 2 shows that the results obtained during the quantitative determination of proline in pure solutions can be regarded as reasonably satisfactory. The results obtained in the presence of traces of hydrochloric acid are twice those obtained in its absence. This fact must be taken into account when calculating the proline content of protein hydrolyzates.

SUMMARY

The proline content of protein hydrolyzates can be determined on the basis of the intensity of the red colored extract obtained on extracting the reaction product formed between proline and ninhydrin with isobutanol.

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BRIEF COMMUNICATIONS

CHROMATOGRAPHIC SEPARATION OF WEIGHABLE AMOUNTS OF CESIUM AND RUBIDIUM ON KU-1 CATION EXCHANGE RESIN

A. A. Pozdnyakov

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, Moscow

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The possibility was demonstrated recently [1] of effecting a rapid and efficient separation of unweighable amounts of francium, cesium, and rubidium on the Russian cation exchange resin KU-1. An interesting feature of this separation was the use of hydrochloric acid at a concentration of 5.5 M as eluant; such a concentration had, up to that time, never been used in the practice of ion exchange chromatography for the separation of the alkali metals. The hydrochloric acid concentration normally used for separating mixtures of these elements lies within the limits 0.1-0.3 M [2]. It was of interest therefore to examine the possibility of separating weighable amounts of rubidium and cesium on this cation exchange resin using hydrochloric acid of varying concentrations for this purpose, and, in addition, to study the efficiency of separation for various proportions of these elements in their mixtures.

Only a few papers have been published on the separation of weighable amounts of the heavy alkali metals [3-6]; in some of these papers the methods described are very long and are not always efficient. There is no published information on the effect of the proportions of rubidium and cesium in test mixtures on separation efficiency.

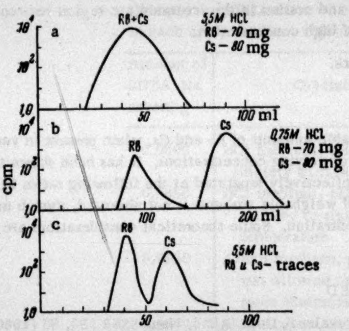

Fig. 1. Elution curves of weighable and trace amounts of Cs and Rb on KU-1 cation exchange resin using HCl solutions of varying acidity.

The method of studying elution of cesium and rubidium labelled with the radioactive isotopes Cs^{134} and Pb^{86} consisted of the following. A column of KU-1 cation exchange resin in the H-form (particle size 150-200 mesh) the column having a diameter of 1 cm and a length of 36 cm was washed with a solution of hydrochloric acid at the test concentration; subsequently 0.1-0.2 ml of an acid solution of the same concentration and containing a mixture of cesium and rubidium was introduced into the top of the column. In order to promote formation of narrow adsorption zones in the column the solution was allowed to pass as slowly as possible along the column, the latter was then eluted with acid of the requisite concentration at the rate of 0.3 ml/min. The solution issuing from the column and having a volume of 1 ml was collected in a test tube and its activity measured on the basis of its β- and γ-radiation respectively on the standard TM-20 counter and on an AMM-4 γ-counter. We decided to use 0.75 and 5.5 M solutions of hydrochloric acid as test eluants; since the greatest difference in the partition coefficients for Rb and Cs, determined under static conditions [11], is observed at these acid concentrations.

Results of experiments on the separation of 80 mg cesium and 70 mg rubidium by means of these solutions are given in Fig. 1, a, b. It follows from this figure that the use of 5.5 M hydrochloric acid as eluant does not even lead to partial separation of cesium and rubidium. Nevertheless, by washing the column with 0.75 M hydrochloric acid we were able to separate these large amounts of rubidium and cesium in about 15 hr. This time can be reduced by passing through the column, after the rubidium has been eluted with 0.75 M hydrochloric acid, an acid solution with a concentration of about 6 M which appreciably accelerates the displacement of the zones of the elements (Fig. 2).

In order to establish the effect of the ratios of weighable amounts of the components on the extent to which they are separated, acid solutions of the concentrations indicated above were used. Results of these experiments are given in Figs. 1 a, b, and 2; it follows from these that separation of both small amounts of one element from predominant amounts of the other for rubidium to cesium ratios of 1: 80 and 70: 1, as well as separation of mixtures containing 150 mg of these elements at a ratio of about 1: 1, is quantitative. This method therefore permits separation of cesium and rubidium in almost any proportion.

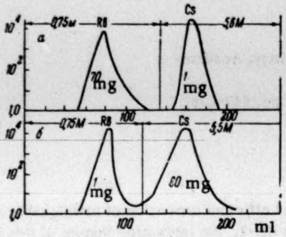

Fig. 2. Elution curves of Cs and Rb for various ratios of these elements in their mixtures.

The fact that weighable amounts of these elements are not separated when they are eluted with high concentrations of hydrochloric acid, while such a separation is effected on eluting with 0.7 M acid solution can be explained by the sharp decrease in the frequency of the elementary acts of sorption and desorption as a consequence of the rapid displacement of the zones of the elements. Nevertheless, the possibility of separating ultrasmall amounts of cesium and rubidium on small columns (10 x 0.3 cm) by means of 5.5 M hydrochloric acid (Fig. 1c) allows one to assume that in addition to the factor mentioned above, the kinetics of the process also affect the efficiency of separation. It is known [2, 7] that the exchange rate is determined by external diffusion in the case of low concentrations, while at high concentrations this rate is determined by internal diffusion. It is obvious that the exchange rate for external diffusion, which is in certain respects identical with the rate of chemical reaction in solution, is higher than in the case of internal diffusion [8, 9]. According to theoretical considerations, in ion exchange chromatography, the increase in the exchange rate of the ions determines the smaller diffuseness of the zones of the elements, i.e., it determines the higher efficiency of separation.

In conclusion, we should like to point out that it would be interesting both from a theoretical and practical point of view to study the efficiency of the separation of rubidium and cesium in the intermediate region between microconcentrations and weighable amounts on eluting with HCl of high concentration.

The author wishes to thank S. S. Rodin for his help in the work.

SUMMARY

A study has been made of the possibility of separating weighable amounts of Rb and Cs, when present in various ratios, on a KU-1 cation exchange resin on eluting them with HCl of varying concentrations. It has been shown that when elution is carried out with 0.75 M HCl, the elements can be effectively separated at the following ratios 1: 1, 1: 80, and 70: 1. When 5.5 M HCl is used for elution, separation of weighable amounts is not observed, though micro amounts of these elements can be separated with acid of this concentration. Some theoretical considerations are advanced to explain these phenomena.

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DESTRUCTION OF ETHYLENEDIAMINETETRACETIC ACID BY OXIDATION WITH HYDROGEN PEROXIDE

P. N. Palei and N. I. Udal'tsova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR, Moscow

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Pribil [1] as well as Smirnov-Averin, Krot, and Sokolov [2] have removed sodium ethylenediaminetetracetate (EDTA-Na) from solution by oxidizing it. Pribil oxidized EDTA-Na by boiling it for a long time in a hydrochloric acid medium with potassium chlorate. Smirnov-Averin et al., recommend the use of a twofold excess of potassium persulfate for oxidizing EDTA-Na; the solution should be boiled for 10-15 min. A drawback of this method of destroying EDTA-Na, however, is the formation of appreciable amounts of sulfate ions in solution, an undesireable feature sometimes. In such cases it is more convenient to destroy EDTA-Na by oxidizing it with hydrogen peroxide. It has been established [3] that excess of concentrated hydrogen peroxide oxidizes ethylenediaminetetracetic acid (EDTA) both in acid and in alkali media; on boiling, oxidation of EDTA is quantitative in 3-5 min. In the cold only about 20% is oxidized in the course of 18-20 hr.

Results of oxidizing EDTA-Na with excess hydrogen peroxide in alkali and acid media at different temperatures are given in the table.

Oxidation of EDTA-Na with Hydrogen Peroxide (ten ml of 30% H_2O_2 was added in each case, the final volume of the solution with 100 ml)

Amount of EDTA-Na taken, g	Oxidizing conditions	EDTA-Na found, g	Percentage EDTA-Na oxidized
0.0360	HCl medium, pH < 1; titrated immediately with $MgCl_2$ solution	0.0354	1.6
0.5860	HCl medium, pH < 1; the solution was allowed to stand for 20-22 hr at room temperature	0.440	24
0.3830	Alkali medium, pH > 10; the solution was allowed to stand for 20-22 hr at room temperature	0.292	21
0.4670	HCl medium, pH < 1; the solution was boiled for 3-5 min	0	100
0.5990	Alkali medium, pH > 10; the solution was boiled for 3-5 min	0	100

Experiment showed that in order to achieve complete oxidation of EDTA-Na not less than a tenfold excess of hydrogen peroxide must be added (with respect to the EDTA-Na).

Destruction of EDTA-Na with hydrogen peroxide can be used with success for separating many elements (Fe^{III}, Th, La, etc.) in the form of their hydroxides from solutions containing the complexon.

The compounds formed during the oxidation of EDTA-Na hardly complex Th, Fe^{III}, and La at all and do not interfere with the quantitative precipitation of their hydroxides. A known amount (20-25 mg) of Th, Fe^{III}, or La in the form of their salts was placed in a beaker, excess EDTA-Na was added (70-200 mg) and the solution diluted

with water to 20 ml; the final solution was neutralized with alkali to pH 10-11, 1-2 ml of 30% H_2O_2 was added and the whole boiled for 3-5 min. The solution was cooled, the precipitate of hydroxides was filtered off, washed, dissolved in acid and the amount of Th, Fe^{III}, or La determined quantitatively by titration with EDTA-Na solution according to published methods [4]. In all cases quantitative separation of the elements as their hydroxides was observed.

Presumably, oxidation with hydrogen peroxide could also be used for destroying EDTA-Na during the separation of many other metals as their hydroxides.

SUMMARY

Hydrogen peroxide completely oxidizes sodium ethylenediaminetetracetate on boiling for 3-5 min in both alkali and acid media. Thorium complexonates are broken down under these conditions; this technique can be used when such elements are separated as their hydroxides.

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4. **Complexometry [in Russian] (Goskhimizdat, Moscow, 1958).**

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

ANALYSIS OF REFRACTORY ALLOYS CONTAINING ZIRCONIUM (TITANIUM) AND TUNGSTEN

O. I. Popova and V. I. Kornilova

Institute of Metalloceramics and Special Alloys, Academy of Sciences Ukr. SSR, Kiev

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Published methods for separating tungsten from zirconium or titanium [1, 2], e.g., fusion with sodium carbonate and subsequent leaching of the melt with water or 10% sodium hydroxide, do not give good results when the contents of the components are high, even after a double reprecipitation.

The aim of the work described here was to develope a method for separating and determining the elements in TiB_2-WC and ZrB_2-WC alloys. The methods which we studied for separating tungsten and zirconium were: 1) separation with perchloric, nitric, and sulfuric acids; 2) separation with cupferron. Separation with acids did give positive results.

Separation by means of cupferron. Tungsten forms complexes with organic acids, in particular with oxalic acid, which dissociate only to a small extent. Titanium and zirconium also form complexes with oxalic acid, but oxalic acid does not interfere with the precipitation of zirconium and titanium cupferronates [3]. For determining the components of the alloys Ti(Zr)−W we thought it would be of interest to extract zirconium and titanium cupferronates [4-6]. We made use of differences in the stability of the complexes of tungsten and zirconium (titanium) with oxalic acid, and in the extractability of their cupferronates, for separating these metals.

TABLE 1. 0.0831 g ZrO_2 and 0.0881 g WO_3 Taken

Oxalic acid taken, g	ZrO_2 found, g
0.45	0.0831; 0.0829
0.90	0.0828; 0.0830
1.35	0.0830; 0.0836
2.25	0.0817; 0.0786

Initially, we made a study of the solubility of zirconium cupferronate in oxalic acid of varying concentrations, in order to establish the minimum amount of oxalic acid required to complex tungsten in the presence of zirconium. The experiments were carried out as follows. Standard solutions of tungsten and zirconium* were poured together, and varying amounts of a concentrated oxalic acid solution added; the zirconium was then precipitated with cupferron (the total volume of the solution was 100 ml). Zirconium cupferronate was filtered off, washed with water, calcined, and weighed.

It follows from the results obtained (Table 1) that zirconium cupferronate does not dissolve in the presence of 0.5-1 g of oxalic acid (this corresponds to 5-10 ml of its saturated solution); the tungsten is readily kept in solution. An appreciable excess of oxalic acid is undesirable; thus when 2.25 g (25 ml of saturated solution) of oxalic acid is taken, zirconium cupferronate also partially dissolves.

Separation of tungsten and zirconium (titanium) by extraction of the cupferronates was checked initially on synthetic mixtures. These experiments were carried out as follows. Standard solutions of tungsten and zirconium or titanium were introduced into a 150 ml separating funnel, 2 ml of concentrated sulfuric acid and 5-10 ml of saturated oxalic acid solution were added and the liquid diluted to 70 ml with water; titanium or zirconium were then precipitated with a 6% aqueous solution of cupferron (7-10 ml). The cupferronate was extracted 2-3 times with chloroform (10, 5, and 5 ml).

After separation, tungsten remains in solution as its oxalate complex; zirconium and titanium pass into the chloroform layer.

Tungsten was determined in the aqueous solution by precipitation with 8-hydroxyquinoline [2, 7]. The solution was neutralized with 20% sodium hydroxide or ammonia to a neutral end point, 15 ml of 2 M sodium acetate was then added – the pH of the solution should be 5 (test with universal indicator paper). Tungsten was precipitated with an acetic acid solution of 8-hydroxyquinoline, the solution was heated to coagulate the precipitate which was filtered off on ashless filter paper (white band) using macerated paper (filter aid). The precipitate was washed 5-6 times with hot water, dried, calcined, and weighed as WO_3.

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* Solutions were prepared from powders of the pure metals. The solutions were standardized gravimetrically.

Titanium was determined in the chloroform layer as follows. Chloroform was removed by gentle evaporation on a water bath or distilled off. The cupferron was destroyed by boiling with a mixture of nitric and sulfuric acids; the mixture was heated until white fumes of sulfuric acid appeared. On cooling, the residue was diluted with water and precipitation effected with cupferron. Results of tungsten and zirconium (titanium) determination, after their separation, are given in Table 2.

TABLE 2.

WO_3 taken, g	WO_3 found, g	TiO_2 taken, g	TiO_2 found, g	ZrO_2 taken, g	ZrO_2 found, g	WO_3 taken, g	WO_3 found, g	TiO_2 taken, g	TiO_2 found, g	ZrO_2 taken, g	ZrO_2 found, g
0,0250	0,0250	0,0140	0,0138	—	—	0,1000	0,0997	0,0420	0,0424	—	—
0,0375	0,0377	0,0210	0,0212	—	—	0,0705	0,0704	—	—	0,0533	0,0535
0,0500	0,0503	0,0280	0,0284	—	—	0,0705	0,0708	—	—	0,0533	0,0534
0,0625	0,0619	0,0350	0,0349	—	—	0,0705	0,0708	—	—	0 0533	0,0533

TABLE 3.

Sample No.	W found, %	W found by the method of additions, %	Ti found, %
1	32,3; 32,2	32,5	48,6; 48,5
2	37,9; 37,7	37,7	43,5; 43,4

As the results given in Table 2 show, by extracting titanium and zirconium cupferronates in the presence of oxalic acid, it is possible to achieve a satisfactory separation of these elements from tungsten, and to determine them separately.

Determination of tungsten and titanium in TiB_2–WC alloys. On the basis of the experiments carried out on synthetic mixtures the following method is suggested for determining titanium (zirconium) and tungsten in alloys.

A 0.1 g aliquot of alloy is dissolved in a mixture of hydrofluoric and nitric acids contained in a platinum basin; sulfuric acid is added, and the mixtures heated to the appearance of white fumes of sulfuric acid. The cooled solution is diluted with water and transferred to a separating funnel; subsequently oxalic acid and cupferron are added. The cupferronate is extracted and the method outlined above for the analysis of synthetic mixtures then followed. Table 3 contains results obtained during the determination of tungsten and titanium in TiB_2–WC alloys.

In order to check on the method, the components of the alloy were determined by the method of additions; satisfactory results were obtained.

SUMMARY

A method has been developed for the determination of titanium (zirconium) and tungsten in TiB_2–WC and ZrB_2–WC alloys. It is based on separation of the elements by precipitation of titanium or zirconium cupferronates in the presence of oxalic acid which masks the tungsten, and extraction separation of the cupferronates followed by determination of tungsten with 8-hydroxyquinoline, and titanium and zirconium by a gravimetric cupferron method.

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A COMPLEXOMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS*

N. I. Zemlyanskii and B. S. Drach

I. Franko L'vov State University

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Original article submitted November 10, 1960

Practical demands for an accurate method which is less difficult than the gravimetric method for determination of phosphorus in phosphoroorganic compounds led us to carry out a careful check on a complexometric method for the determination of orthophosphate. For study we chose the simplest method based on precipitation of PO_4^{3-} as $MgNH_4PO_4$ with subsequent determination of the magnesium in the latter by a back complexometric titration [1-5]. On using the normal method for complexometric determination of phosphates [1, 5] involving a single precipitation of $MgNH_4PO_4$, it was found that the results for orthophosphate determination were not reproducible and were very high. The relative error amounted to +5.0%. Modifying the precipitation conditions for $MgNH_4PO_4$ [precipitation temperature, amount of excess magnesia mixture, ammonium chloride concentration, addition of sodium ethylenediaminetetracetate (EDTA-Na)] does not lead to satisfactory results [4-6]. Moreover, during back titration of excess EDTA-Na with a magnesium salt using eriochrome black T as indicator, the color change is less distinct than during direct titration. The color change is observed over a range of 0.10-0.12 ml on titrating with 0.1 N magnesium salt solution.

TABLE 1. Complexometric Determination of Orthophosphate

P_2O_5, mg		Mean error relative, %
taken	found	
165,8	166,1; 165,0; 165,1	—0,24
186,6	186,0; 186,1; 186,6	—0,21
207,3	208,0; 208,1; 207,6	+0,29
228,0	227,6; 228,2; 228,6	+0,04
248,8	248,1; 248,1; 249,3	—0,12

Experiments showed that by carrying out a double precipitation of magnesium ammonium phosphate, and also by titrating with a mixed indicator, accurate and reproducible results can be obtained for orthophosphate.

The use of a mixture of eriochrome black T with methyl orange or methyl red as a mixed indicator has been described [7, 3]. In the work described here we used a mixture of eriochrome black T and p-nitrosodimethylaniline as the mixed indicator for the complexometric titration of magnesium, this mixed indicator gives a distinct color change from green to reddish. Before completion of titration a gradual weakening of the green color is observed. At the end point, on adding the last 0.02-0.04 ml of 0.1 N magnesium salt solution, the green color changes distinctly to reddish. p-Nitrosodimethylaniline does not affect titration. Results for phosphate determination are most accurate when the EDTA-Na solution is standardized against an aliquot of potassium dihydrogen phosphate using the same technique as in an actual determination.

Table 1 contains results for the complexometric determination of orthophosphate using the new indicator – mixture of eriochrome black T and p-nitrosodimethylaniline – and a double precipitation of $MgNH_4PO_4$ and an EDTA-Na solution whose normality had been established against an aliquot of potassium dihydrogen phosphate.

EXPERIMENTAL

150-250 mg of $MgNH_4PO_4$ after the usual reprecipitation and standing, is filtered through a No. 3 or No. 4 glass filter, thoroughly washed with 2.5% ammonia solution and dissolved in 30-35 ml of hydrochloric acid 1 : 5. The filter is carefully washed with twice distilled water. Fifty ml of 0.1 N EDTA-Na is added to the filtrate and the solution is then made alkaline with concentrated ammonia to the blue color of litmus paper. Fifteen ml of ammoniacal buffer solution, with pH 10 is added and the solution diluted to 200-250 ml with twice distilled water. The solution is cooled to 5-10° and a solid mixture of eriochrome black T and NaCl (1 : 500) added on a knife tip until a moderate blue color develops, 8-10 drops of 0.005% aqueous p-nitrosodimethylaniline is then added until

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* We wish to thank R. N. Golovat for valuable advice given in the course of this work.

an emerald-green color is obtained. The solution is titrated with 0.1 N magnesium salt solution until the green color has disappeared completely and a reddish color is obtained. The magnesium salt solution is standardized by titrating with EDTA-Na solution using the mixed indicator, the EDTA-Na solution having been standardized against an aliquot of potassium dihydrogen phosphate.

The method developed has been used for determining phosphorus in phosphoroorganic compounds. An aliquot of the phosphoroorganic compound was oxidized with a mixture of hydrogen peroxide (free from phosphates) and concentrated sulfuric acid; PO_4^{3-} ions were precipitated as $MgNH_4PO_4$ and after reprecipitation of the latter, determination was carried out as described above. When less than 100 mg of $MgNH_4PO_4$ was obtained, 0.05 N solutions of EDTA-Na and magnesium salt were used.

TABLE 2. Determination of Phosphorus in Some Phosphoroorganic Compounds

Compound	P, %	
	calc.	found
$(C_2H_5O)_2P(S)SK$	13,81	13,78; 13,77; 13,76; 13,82; 13,80; 13,85
$[(i-C_3H_7O)_2P(S)S]_2$	14,52	14,58; 14,50; 14,57
$(C_6H_5O)_2P(S)SH$	10,97	10,93; 10,94
$(C_6H_5O)_2P(S)SK$*	9,67	9,70; 9,65; 9,71

*M. p. 187-188°. This compound was prepared by the interaction of O,O-diphenyldithiophosphoric acid and K_2CO_3 in an ether medium. The product was purified by precipitation with benzene from concentrated acetone solutions.

The method gives readily reproducible results. The accuracy is about 0.3% (relative). Table 2 contains the results for phosphorus determination in some carefully purified phosphoroorganic compounds.

SUMMARY

A more precise complexometric method of determining PO_4^{3-} has been applied to the determination of phosphorus in organic compounds. Results with a relative error of 0.3% have been obtained on reprecipitating the $MgNH_4PO_4$ precipitates, standardizing the EDTA-Na solution used against orthophosphate, and using a mixed indicator consisting of eriochrome black T and p-nitrosodimethylaniline.

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REVIEWS AND BIBLIOGRAPHY

ORGANIC REAGENTS IN ANALYTICAL CHEMISTRY

Transactions of the Commission on Analytical Chemistry, Academy of Sciences of the USSR, Volume XI. 462 pp. Izd. AN SSSR, Moscow, 1960. Printing 4000. Price 20 rubles (old denomination).

V. A. Nazarenko

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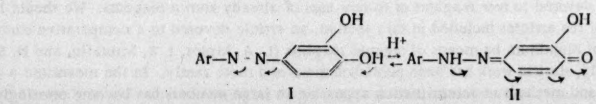
September-October, 1961

Volume XI of the Transactions of the Commission on Analytical Chemistry is a collection consisting of 47 articles by different authors on problems relating to the theory of the action of organic reagents and their use in analysis. The articles are divided into three sections: 1) theoretical research and study of organic reagents; 2) methods for determination of individual elements; and 3) different applications of organic reagents. The contents of the articles do not always justify the basis for such a strict subdivision.

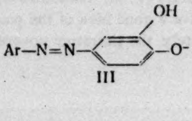
In the opening article of the symposium, "The Effect of the Nature of the Chromophore on Functional-Analytical Groups," the author of the article, M. Z. Yampol'skii, correctly points out the deficiency of the concept of functional-analytical groups for explaining the mechanism of color reactions without taking into account the nature of the chemical bond in the reagent molecule. Nevertheless, the effect of a chromophore on the capacity of an organic compound to be a color reagent for a metal ion is only stated in the article, and is not subjected to actual consideration. The author still adheres to the abandoned concept of the chromophore as a coordinately-unsaturated atom, which did not allow him to come to the obvious conclusion that an organic compound can give a color reaction with a metal ion, only when the reactive group of the reagent closely adjoins the conjugated chain of the chromophore or is a part of the latter.

V. I. Kuznetsov in the article "The Mechanism of Acid Decomposition of Complex Salts," considers phenomena observed in solutions of colored cyclic salts on increasing the hydrogen ion concentration. On slow acidification of a solution of a colored cyclic salt with a strong mineral acid, the color gradually approximates to that which is characteristic for a strongly acid solution of the reagent. When, however, the mineral acid is added rapidly, the color deepens strongly, this color being stable for a more or less prolonged period. Considering the difference between the color of a cyclic salt and that of a reagent as a consequence of intramolecular ionization, V. I. Kuznetsov explains this phenomenon by the fact that "acid decomposition of cyclic salts is preceded by a state with a very strongly manifested intramolecular ionization." This explanation, which is, unfortunately, based on qualitative visual observation, is not convincing. The phenomenon observed can also be explained from another viewpoint. In all the numerous examples given in the article, the reagents used are hydroxyazo compounds for which tautomeric hydroxyazo—quinohydrazone transformations leading to a simultaneous change in the chromophore and reactive group are characteristic, e.g., for derivatives of 3,4-dihydroxyazobenzene (I, II).

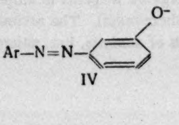


I II

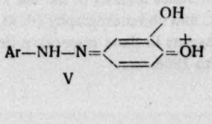
Compound II which possesses a carbonyl oxygen with an unshared electron pair, is more capable of forming a coordination bond with a metal ion than in compound I. During rapid decomposition of the cyclic salt formed by compound II, there immediately appears a large amount of unstable molecules of this compound, while its color, as is quite evident, will not be identical with the color of compound I or ions III and IV existing in alkaline media, and of ion V existing in a strongly acid medium



III



IV



V

In passing, we should point out that not only this case, but often other phenomena which are explained from the position of the hypothesis of intramolecular ionization, or where this theory is used as a basis, can be given other interpretation which are more in line with modern color theory. It is quite obvious that the "hypothesis of intramolecular ionization" requires quantitative physicochemical proof.

In another article "The Mechanism of the Color Reactions of Boron with Hydroxyanthraquinones," V. I. Kuznetsov establishes that in a medium of almost concentrated sulfuric acid, boron reacts with hydroxyanthraquinones as a cation. This fact explains the resemblance of the boron reaction with similar reactions of other multivalent elements undoubtedly present in strongly acid media as cations (germanium, zirconium). However, what was said in the previous instance is also applicable to a certain extent, to the further explanation of the mechanism of the color reactions of boron with hydroxyanthraquinones in concentrated sulfuric acid. Reactions of boron with hydroxyanthraquinones are preceded by a change in the chromophore of the latter caused by the breaking of the hydrogen bond between the carbonyl oxygen and the hydroxy group in the α-position. The explanation of the mechanism of the color reactions of boron with hydroxyanthraquinones given in the article by P. N. Palei, A. A. Nemodruk, and Z. I. Pyzhova in the second section of the symposium (p. 227) is also insufficient, since the authors consider that the complexing agent is not the boron cation, but metaboric acid, and they do not take into account the preceding reaction of the change in the chromophore of the reagent, while the color change is ascribed only to polarization of the bond of the central atom with the hydroxyl oxygen of the addendum. One cannot deny the effect of intramolecular ionization or bond polarization on the color of the intra complex compound. But, however strongly these effects may be manifested, the reason for the development of "not-comparable" colors are not these phenomena, but the preceding reactions involving changes in the chromophore of the organic reagent.

In V. B. Avilov's article the author points out that during potentiometric studies of complex formation between metal ions and the anions of weak organic acids, a correct characteristic of the behavior of redox systems in actual cases is only possible when one takes into account the effect of all the reagents used, in particular that of the strong acids, on the potential of the system.

Taking phenolphthalein as an example, I. G. Shafran critically examines the theory of the use of one-color indicators and defines theory more accurately in the case where a doubly charged indicator ion is colored.

A large group of articles in the first section is devoted to consideration of the analytical properties of, and the application of individual groups of organic reagents. As examples of a quantitative approach to the study of organic reagents, of particular interest is the work carried out by V. M. Peshkova and A. P. Zozulin, and also by A. L. Gershuns; while the work carried out by A. I. Cherkesov serves as an example of the search for reagents on the basis of modern theories of the structure and color of organic compounds, and the work of A. I. Busev and M. I. Ivanyutin for the wide range of materials studied.

The article by I. M. Korenman, A. A. Tumanov, and Z. V. Krainova which ends the first section of the syposium, demonstrates the simplicity and applicability of the radioactive isotopes method for studying precipitation and coprecipitation of elements by the action of organic precipitants, the hydroxyquinolates of zirconium, copper, and cobalt being taken as test examples.

Articles on the use of organic reagents for determination of individual elements are collected in the second section. These articles are devoted to new reagents or to new uses of already known reagents. We should like to mention in particular one of the articles included in this section, an article devoted to a comparative study of methods for determining traces of aluminum by means of organic reagents (L. A. Molot, I. S. Mustafin, and N. S. Frumina). In recent years, unfortunately, similar work has been published more and more rarely. In the meantime a critical evaluation of new reagents and methods of determination appearing in large numbers has become pressingly urgent, since the analytical chemist will simply become confused, unless the new methods are not based on a critical evaluation of the possible variants, as has been done in the article by A. K. Babko and L. V. Markova which deals with reactions for sulfate ions (p. 309).

The third section includes a short article by R. Pribil on new achievements in complexometry with new and interesting examples from an analytical point of view of the selectivity of complexometric determinations. This section also includes reviews of the use of organic reagents in amperometry (V. M. Vladimirova), polarography (S. I. Sinyakova), and chromatography (F. M. Shemyakin). The reviews give a good idea of the possibilities of the use of organic reagents in these respective fields of analysis, but, unfortunately the literature covered in these fields only extends to 1956.

In an article on the selectivity of ion exchange resins, M. M. Senyavin, G. M. Kolosova, and A. B. Pashkov consider the physicochemical processes which occur during ion exchange, and show that the selectivity of the action of ion exchange resins is determined not only by the nature of the functional groups but also by the structure of the sorbent.

The third section also includes several articles on the use of organic reagents for the determination of organic compounds: ethylene oxide (E. Sh. Groisberg); dinitroethylene glycol (A. A. Belyakov); aniline, methylaniline, and dimethylaniline (A. A. Belyakov and N. V. Gorbyleva); esters of p-nitrobenzoic acid (L. P. Kuliev and P. V. Kristalev), air contaminating products from the industrial production of carbon tetrachloride (A. Ya. Tubina); practical recommendations are given. The disproportionately small number of articles from this section included in the symposium only serves to emphasize that the analytical research worker has not hitherto given due attention to this important branch of analytical chemistry.

It is impossible in such a short review to characterize sufficiently fully about fifty various articles. Each of them is of more or less theoretical or practical interest. The symposium will be useful for chemists working in the respective fields.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. –Publisher.

ANALYTICAL CHEMISTRY AND THE TWENTY-SECOND CONGRESS OF THE COMMUNIST PARTY OF THE SOVIET UNION

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 657-659, November-December, 1961

The twenty-second Congress of the Communist Party of the Soviet Union will sum up socialist construction in our country and will indicate the path to be taken for constructing a communist society.

In connection with the wide development of a communist structure important new problems confront analytical chemistry just as they confront other sciences.

Of no little importance in the development of analytical chemistry in the Soviet Union has been the successful development of the theoretical bases of analytical methods, and the development of the theory of the analytical chemistry of individual elements in Mendeleev's Periodic Table. A considerable amount of work has been carried out in developing rapid and accurate methods of qualitative and quantitative determination of any amounts of elements and compounds independently of the presence of other elements. Important results have been achieved in the search for new possibilities of controlling chemical reactions underlying analytical methods. Research work along these lines has been concentrated on studying chemical equilibria, on the effect of varying conditions on the path of chemical reactions and the stability of the simple and complex compounds formed, on studies of redox potentials, formation of compounds insoluble in a given medium, and colloid formation, and on the study of the structure of indicators and the nature of the color of compounds. One must point out the successful development in our laboratories of the theory and practice of the use of organic reagents in analysis, the development of extraction methods and ion exchange, and also the study of coprecipitation mechanisms. The wide use of the latest achievements in molecular physics, electron optics, radiochemistry, and sorption techniques, play an important role in developing all these problems.

In recent years systematic studies have been successfully carried out on chemical reactions of individual elements, mainly of the rare and scattered elements by modern physicochemical methods from the point of view of the demands placed on them by analytical chemistry. This has made it possible to change over from developing individual analytical methods, from solving special problems in the analytical chemistry of an element to developing a theory for the analytical chemistry of an element, to generalization of factual material, i.e., to creating a scientific basis for current and newly developed analytical methods. The chemical similarity and differences between elements in different valence states are being studied more thoroughly on the basis of the periodic law.

One must emphasize the need for further development of material (phase) analysis and of systematic organic analysis on the basis of the latest achievements in the field of the determination of functional groups. Inorganic phase analysis and organic analysis are still one of the least developed branches of analytical chemistry. At the same time phase analysis is of great importance for mineralogy, metallurgy, metal treatment, the silicate industry, and the technology of certain industries, for which ordinary chemical analysis is not adequate, while information on the real forms of compounds in natural and technical materials is needed.

Analytical chemistry is of exceptional importance for the various natural sciences and for the control of modern production. At present analytical methods play a particularly important role in the study of the conversion of certain materials into others. Such analytical methods as radioactivation analysis, mass-spectroscopy, spectographic analysis, and spectrophotometry, have played an important part in organizing and improving the production of pure and superpure materials in modern metallury, for which the use of the so-called rare and scattered elements is a characteristic feature. Analytical methods have acquired great importance in the study and development of natural sources of raw material. The geological service has at its disposal at present a well developed chain of splendidly equipped laboratories of different types. Production control is of great importance in the chemical, atomic, power, petroleum, pharmaceutical, food and other branches of industry. Analytical chemical control has played an exceptionally important part in improving many industries.

Analytical chemical control and analytical chemical methods are developing with increased tempo in conjunction with the creation of more highly efficient and economically profitable methods of high tonnage organic synthesis—development of natural and byproduct gases, coal, petroleum, various plant wastes—which makes it possible to obtain starting materials for the synthesis of polymeric and other materials. Nevertheless, the analysis of organic materials is characterized by the methods required and has still not been developed sufficiently to be separated from organic chemistry.

The expansion of research in the fields of the rare elements and semiconducting materials, the preparation of plastic and other high molecular weight materials, the solution of problems relating to the production of synthetic materials with given properties have demanded that analytical chemists develop theory further and develop new analytical methods.

Analytical chemistry has played its part in agricultural chemistry—including such important natural reserves as soil (microelements, fertilizer analysis, etc) plant and animal materials—and also in the study of metabolism in the organism without destroying the totality of the functioning living tissue and without halting the living processes and interfering in their function. The production of antibiotics, vitamins, and other physiologically active materials would be impossible without a well established analytical chemical control.

The large volume of production control and the short time within which it has to be carried out have compelled analysts to search for new ways of speeding up work in analytical laboratories. With the ever increasing number of elements for which production control is necessary, demands for increasing accuracy and tempo can only be satisfied by developing selective reactions and methods, which can be carried out without removing the elements which normally interfere, and which enable systematic classical analysis to be avoided.

One must note the undoubted successes achieved in ensuring maximum automation of actual analytical methods based on spectrographic analysis, spectrophotometry, electrochemical methods, and the use of radioactive indicators. This in turn has opened up the way to automatic analytical chemical control of production processes.

Solution of new problems would be impossible without essentially improving the training of cadres of analytical chemists and increasing their number. The respective departments in the universities have carried out a lot of work along these lines.

Such important branches of industry as the metallurgical, atomic, aviation, and petroleum industries have at their disposal modern, well equipped laboratories. Production of pure and specially pure reagents in the required amounts has been organized.

A large amount of scientific and scientific-technical literature is published in our country on analytical chemistry. Among them one must point out the series of monographs on the analytical chemistry of the most important elements, the textbooks on the analysis of pure materials and on the analytical chemical control of production.

Analytical chemistry is developing very rapidly in the USSR and strongly influences the progress of other natural sciences and technical production. In the last ten years an outstanding analytical school has arisen which is developing new progressive theories and is giving many valuable practical results.

Soviet scientists inspired by the Communist Party, shoulder to shoulder with all the workers in our country raise the bright edifice of communism. Together with the whole nation they subjugate and overwhelm nature, use its powerful forces in the interest of peace and progress, and create huge material and spiritual values. There is no doubt that the ranks of scientists will grow and strengthen, supplemented by new cadres, who will make our country famous and enrich its advanced science with new, outstanding achievements and discoveries.

THE EFFECT OF THE DEGREE TO WHICH TEST MATERIAL IS GROUND ON THE RESULTS OF QUANTITATIVE SPECTROGRAPHIC ANALYSIS BY THE BLAST METHOD

G. I. Kibisov and N. B. Kubasova

State University of Applied Chemistry, Leningrad

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The possibilities of the air blast method [1-5] which we have successfully used for three years in a somewhat modified form for quantitative analysis have been confirmed by daily practice. Several hundred analyses have been carried out, in the main only in the State Institute of Applied Chemistry (SIAC). Several institutes and plants have adopted the general features of the SIAC method [2]. In this connection the article by Raikhbaum and Luzhinova[3] has evoked considerable interest. The authors of this article established that there is a strong relationship between line intensity and the extent to which the test material has been ground when the spectra are excited by the spraying–blast technique of Rusanov in an AVR-2 apparatus [5]. This fact testifies to incomplete evaporation of particles in the arc discharge. When the particles have been ground very finely they coagulate again, and the effect does not disappear [3]. Since accurate reproducibility and control of the granular composition of the test material are impossible under analytical conditions, it follows from [3] that it is doubtful whether or not the blast method can be used successfully for quantitative analysis.

The characteristic feature of the blast method used in SIAC is the introduction of the powdered material into the arc by means of an air stream [2]. We have examined the relationship between line intensity and the extent to which the powder has been ground. For this purpose test materials of the slag type were sintered with oxidizing agents [4] and the product obtained ground and then sieved. Two types of powders were prepared which differed from each other in the way in which the internal standard was introduced. In one case the internal standard (cobalt) was introduced before sintering, and, consequently, before grinding, while in the second case the internal standard was introduced after the test material had been finally ground. The ground samples were diluted five times with carbon powder sieved through a No. 32 sieve.

The spectra were photographed in a medium type spectrograph at a current of 15 amps under standard conditions [2]. Lines used in slag analysis were measured photometrically. The relationship between line blackening and the value of ΔS on the degree of grinding are given in the tables.

Initially, experiments were carried out with powders ground in a mortar and sieved through various sieves. Cobalt in the form of aliquots of Co_2O_3 was introduced separately after grinding to each fraction. The results are given in Table 1.

In order to give an idea of the reproducibility of ΔS values, when photographs were taken in parallel, the table, in addition to containing abridged results for various elements, contains detailed factual material on manganese. It follows from the table that the line intensity of all elements increases with decreasing size of particles passing into the arc discharge. In this connection there occurs a sharp increase in the value of ΔS. Since we did not have very fine sieves it was not possible in the course of this experiment to follow changes in line intensity, when the test material was ground even finer. Accordingly, we carried out an additional experiment, results of which are given in Table 2. In this case, the material, after sintering, was divided into seven parts and each part ground in an IS apparatus for 1.5 to 20 min. Cobalt was introduced after grinding.

It follows from Table 2 that test material is ground to a very fine state in the IS apparatus in 2.5-3 min, while the intensity to a very fine state in the IS apparatus in 2.5-3 min, while the intensity and also the ΔS values hardly change at all even when the test material is treated for a considerably longer time. The small increase in the line intensity of silicon can probably be attributed to contamination of the test material by a plastic material from which the boat in which the material to be ground is placed. The experiments described convincingly demonstrate that the analytical results obtained when the blast method is used will not depend on the degree to which test material has been ground, as long as the fineness of grinding exceeds a certain value which can be achieved in practice in an IS apparatus.

TABLE 1

Sieve size, mm	S Mn	S Co	ΔS Mn	ΔS_{mean} Mn	S Fe	ΔS_{mean} Fe	S Al	ΔS_{mean} Al	S Si	ΔS_{mean} Si	S Ca	ΔS_{mean} Ca
0,125	52	116	—064	—0,66	29	—0,84	62	—1,10	38	—1,33		
	55	125	—0,70		32		69		48			
	41	105	—0.64		21		51		28	—	—	
0,100	60	95	—0,35	—0,38	33	—0,68	90	—0,75	50	—1,15	20	—1,46
	67	104	—0,37		34		94		55		23	
	67	108	—0,41		36		94		53		24	
0,074	113	111	0,02	0,01	65	—0,43	145	—0,34	85	—0,95	64	—1,18
	115	115	0,00		67		150		91		65	
	118	117	0,01		77		153		90		68	
0,063	131	113	0,18	0,16	87	—0,25	167	—0,14	101	—0,83	81	—1,01
	123	—	—		86		167		100		79	
	122	107	0,15		84		170		96		81	
0,056	149	104	0,45	0,45	98	—0,01	193	0,21	106	—0,65	100	—0,73
	147	100	0,47		101		191		106		99	
	150	106	0,44		101		195		110		99	
0,044	168	111	0,57	0,56	124	0,15	210	0,34	129	—0,51	113	—0,67
	165	110	0,55		125		210		122		108	
	162	107	0,55		122		210				107	

TABLE 2

Grinding time, min	S Fe	S Co	ΔS Fe	ΔS_{mean} Fe	S Mn	ΔS_{mean} Mn	S Al	ΔS_{mean} Al	S Si	ΔS_{mean} Si	S Ca	ΔS_{mean} Ca
1,5	53	110	—0,57	—0,57	83	—0,27	86	0,48	66	—0,59	38	—0,95
	47	98	—0,51		75		82		64		36	
	52	114	—0,61		83		87		73		39	
2	112	107	0,05	0,05	152	0,48	151	1,23	107	—0,23	95	—0,38
	111	107	0,04		155		156		112		93	
	108	103	0,05		153		152		108		95	
2,5	98	97	0,01	0,01	142	0,45	147	1,34	102	—0,27	92	—0,37
	106	107	—0,01		152		156		109		100	
6	98	101	—0,03	—0,04	143	0,42	154	1,31	113	—0,17	90	—0,42
	101	106	—0,05		148		158		117		90	
8	98	99	—0,01	0,02	142	0,42	150	1,30	110	—0,16	87	—0,44
	97	93	0,04		136		149		115		82	
	102	99	0,03		142		154		116		88	
13	93	104	—0,11	—0,12	140	0,37	153	1,25	116	—0,13	88	—0,43
	98	109	—0,11		147		158		122		90	
	97	111	—0,14		147		158		120		91	
20	97	103	—0,06	—0,06	141	0,38	156	1,31	118	—0,15	83	—0,48
	100	106	—0,06		144		160		121		88	
	107	113	—0,06		151		166		122		—	

It was of interest to follow the change in ΔS values in those cases where the internal standard was introduced before sintering, and accordingly, was subjected to grinding at the same time as the bulk of the test material. Table 3 contains the results of such an experiment. Each of samples 1-6 is a powder which passed through a given sieve but was retained on the next, finer sieve. These samples were prepared by grinding the powder in a mortar. Samples 7-9 were prepared by grinding fraction 6 in an IS apparatus for 4, 7, and 10 min, respectively.

TABLE 3

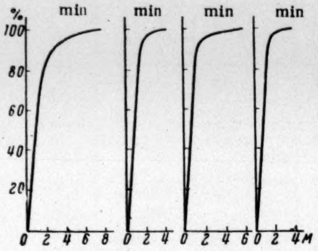
Sample no.	Sieve size,min	S_{Mn}	$\Delta S_{mean\,Mn}$	S_{Fe}	$\Delta S_{mean\,Fe}$	S	$\Delta S_{mean\,Al}$	S_{Si}	$\Delta S_{mean\,Si}$	S_{Ca}	$\Delta S_{mean\,Ca}$
1	0,12	16 12	−0,12	10 7	−0,18	37 31	−0,45	13 13	−0,67	— —	—
2	0,125	51 52	−0,25	25 27	−0,50	85 91	−0,59	39 42	−1,07	21 21	−1,26
3	0,100	71 72	−0,29	36 38	−0,66	94 93	−0,59	51 50	−1,02	35 35	−1,17
4	0,083	97 103	−0,30	51 56	−0,76	101 102	−0,62	59 64	−1,06	53 59	−1,07
5	0,056	118 129 127	−0,29	75 84 83	−0,73	90 101 97	−0,62	61 72 66	−0,92	74 80 80	−0,85
6	0,044	122 114 115	−0,30	83 76 76	−0,69	94 79 85	−0,60	65 53 53	−0,89	75 69 71	−0,74
7	—	102 97 82	−0,33	71 66 56	−0,64	95 98 102	−0,49	58 55 53	−0,92	57 58 45	−0,94
8	—	90 88 85	−0,32	50 48 46	−0,72	90 97 98	−0,47	51 53 53	−0,89	49 50 48	−0,93
9	—	85 91 97	−0,30	44 47 53	−0,73	94 99 101	−0,45	49 55 57	−0,89	48 50 54	−0,92

It is clear from Table 3 that it is also possible, when an analysis is carried out, to introduce the internal standard before sintering, since after treatment of the test material in an IS apparatus, the ΔS values for all the elements tested becomes independent of the grinding time. For analytical purposes, it is more correct to introduce the internal standard before sintering, since cobalt should be distributed more evenly in the test material when this technique is employed, while the ΔS values will be independent of the degree of grinding over wider limits.

Thus, all the experiments carried out show that after the particles have been ground to a certain fineness, the line intensity of Mn, Fe, Si, Al, Ca, and Co, within the limits of experimental error, remains constant and is independent of a further increase in grinding time. An attempt was made to estimate the degree of grinding of test material by measuring the particle size on a MIP-4 polarizing microscope at a magnification of × 720. Shapeless aggregates of very weakly aggregated particles as well as individual particles were visible in the field of vision of the microscope. At lower magnifications it is readily seen that when the aggregates are touched slightly adhesion of the particles is destroyed. Powders ground in the IS apparatus for 1.5, 3.5, 8, and 13 min were examined under the microscope. Results of measuring a large number of individual particles are presented in the diagram. It follows from these curves that approximately half the particles have a diameter of down to 1 μ, while 90%, of all the particles have a diameter between 1.5 and 2 μ. The granular state of the powders was very homogeneous, as long as one does not take into account the powder obtained on grinding for 1.5 min. Apparently, grinding for more than 3 min only increases the fineness very little, while the line intensity hardly increases at all after 2-3 min grinding.

It can be assumed that the very unstable, friable accumulations of particles observable under the microscope are destroyed just by mixing the ground powder with carbon powder. The latter is not ground in the IS apparatus but is prepared by grinding carbon electrodes with a cutter and then sieving the powder through a coarse No. 32 sieve.

During vigorous mixing with the ground sample in a mixer, these coarse particles of carbon powder should affect the material being ground and break down the aggregates of particles of the sample. The air blast should have the same effect. Accordingly, the fraction of aggregated particles in the total mass of the powder, is presumably, insignificant, and the evaporation of the test material is determined by the individual particles. Whether or not particles of diameter up to 2 μ evaporate completely during their passage through the arc flame is a question which can only be solved from indirect signs. Should the fraction of aggregated particles be high, while the aggregates and individual particles only succeeded in partially evaporating, the line intensity and ΔS values would vary so strongly, that quantitative analysis would be impossible; this is not observed in practice. Accordingly, we suggest that complete evaporation of the overwhelming majority of the particle occurs in an arc discharge.



The relation between the granular state of powders and grinding time in the IS apparatus.

One can conclude that the results of analyzing materials of constant composition by the blast method are independent of the degree to which the samples and standards have been ground, as long as a certain degree of fineness readily achieved in practice is ensured.

SUMMARY

When spectra are excited by the blast method, line intensity is dependent on the degree to which test material has been ground. When the material is very fine (when not less than 90% of all the particles have a diameter not exceeding 2 μ) particle size no longer affects the analytical results. An instrument is recommended which ensures that powders are ground to the requisite fineness in 2-4 min.

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THE MUTUAL INFLUENCE OF THE ALKALI METALS DURING THEIR DETERMINATION BY FLAME PHOTOMETRY

T. F. Borovik-Romanova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Other elements which are present in the flame affect the radiation intensity of a test element. In the case of the alkali metals this effect is most strongly shown in the case of the radiation intensity of Cs, Rb, and also K; the effect is much weaker for Na and is almost completely absent in the case of Li.

It is desirable to establish what is the order of the change in intensity one can expect in each separate instance, and also to establish the reasons for such changes. There is an appreciable amount of published material on this question; this refers mainly to changes in the radiation intensity of sodium, potassium, and lithium [1-29]. The work described here is also devoted to a study of the mutual effect of alkali metals when working with a flame. A series of experimental results is given, while an attempt is also made to calculate the magnitude of this effect on the basis of theoretical premises.

The work was carried out with an air-acetylene flame using an atomizer and a burner of the Zeiss type. A FÉU-22 photomultiplier was fitted directly onto the outlet slit of an UM-2 monocrhomator and a voltage of 1100-1200 v was applied to the photomultiplier from a high voltage stabilized rectifier. The current which developed was measured with a mirror galvanometer having a sensitivity of 10^{-9} amp/mm. The flame was arranged at a distance of 10-12 cm from the monocrhomator slit at such a height that the blue cone of the flame was 10-12 mm lower than the slit; the width of the inlet and outlet slits was 0.10 mm. The following lines were used for measurement: for Li, 670.8 mμ; Na, 589.3 mμ; Rb, 780.0 mμ; Cs, 852.1 mμ. The following experiments were carried out.

1. A study was made of the change in radiation intensity of lithium, sodium, rubidium, and cesium at a concentration of 10 mg/liter on adding 5000 mg/liter of KCl to each of the solutions. The ratio I/I_0 was taken as a measure of the effect of this mutual influence, where I is the intensity of the radiation of the test element when KCl has been added, and I_0 the intensity in the absence of potassium, as was done during a study of the effect with a dc arc [30]. For similar experimental conditions the ratio I/I_0 is a reasonably constant value.

It follows from Table 1 that the effect is greater the higher the atomic weight of the test element, the difference being very great: there is a hardly observable change in the intensity of the lithium line at 670.8 mμ on adding KCl; the intensity of the cesium line (852.1 mμ) on the other hand increases 27 times.

TABLE 1. Effect of 5000 mg KCl/liter on the Radiation Intensity of Li (670.8 mμ); and Rb (780.0 mμ), and Cs (852.1 mμ); taken from experimental results

10 mg/liter of the element taken	Ratio of intensities I/I_0
Li	0.99
Na	1.2
Rb	9.1
Cs	26.9

TABLE 2. Effect of 5000 mg KCl/liter on the Radiation Intensity of Rb (780.0 mμ), Introduced into the Flame in the Form of RbCl, $RbNO_3$, and Rb_2SO_4

10 mg Rb/l taken in the form of	Effect of KCl at a concentration of 5000 mg/liter
RbCl	9.10
$RbNO_3$	9.04
Rb_2SO_4	8.99

2. In subsequent experiments we established the effect of various concentrations of KCl and NaCl (50, 500, and 5000 mg/liter) on the radiation intensity of rubidium at a concentration of 10 mg/liter, and also studied the effect of the same KCl or NaCl content (5000 mg/liter) on the radiation intensity of Rb at various concentrations of the latter (10, 20, 30, 40 mg/liter). The results obtained are given in Figs. 1-4*. It is clear from the curves that on increasing the KCl and NaCl concentration from 50 to 5000 mg/liter, their effect on the intensity of the Rb line increases; the increase in intensity being greater on adding KCl than on adding NaCl. At low rubidium concentration, the calibration curve has a parabolic shape (similar calibration curves are also obtained at low Cs and K concentrations).

As the concentration of the element added is increased the radiation intensity of Rb increases and the curve straightens out. At a KCl (or NaCl) concentration of 5000 mg/liter the curves are linear. In order to demonstrate more clearly the relation between the effect of 5000 mg/liter of KCl and NaCl on the radiation intensity of rubidium and the concentration of the latter, curves are shown in Figs. 3 and 4 which are constructed within the coordinates $C-I/I_0$. These curves show that on increasing the Rb concentration from 10 to 40 mg/liter while the same amount of KCl or NaCl is added, the effect weakens.

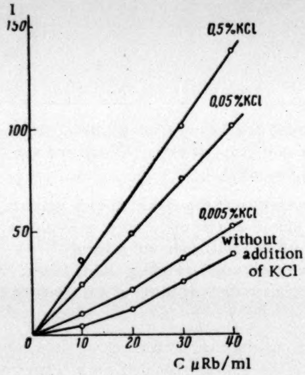

Fig. 1. Calibration curves for Rb (780.0 m μ) with and without addition of varying amounts of KCl.

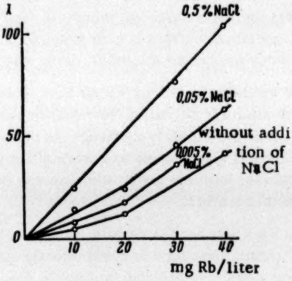

Fig. 2. Calibration curves for Rb (780.0 m μ) with and without addition of varying amounts of NaCl.

3. KCl at a concentration of 5000 mg/liter was added to three solutions of rubidium introduced into the flame in the form of different compounds RbCl, $RbNO_3$, and Rb_2SO_4 at concentrations of 10 mg/liter—calculated as rubidium. The effect was the same for all three compounds (Table 2).

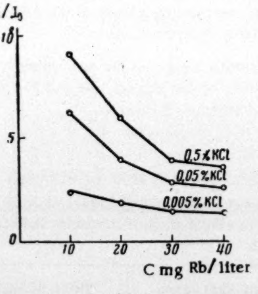

Fig. 3. Effect of equal amounts of KCl on the radiation intensity of various amounts of Rb (780.0 m μ).

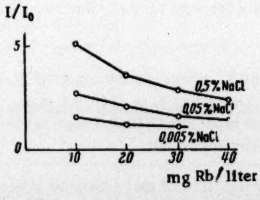

Fig. 4. Effect of equal amounts of NaCl on the radiation intensity of various amounts of Rb (780.0 m μ).

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*When this work had been finished and had been sent for publication, the article by Fabrikova appeared [31]; this article contained calibration curves similar to those given in Figs. 1 and 2 for Rb concentration from 0 to 100 mg/liter without addition of potassium, and with addition of 500, 1000, and 2500 mg potassium/liter.

Discussion of Results. The reasons leading to changes in the radiation intensity of the test elements in the presence of other elements may be of three types [13,33].

1. Interference which arises from the radiation of the flame and from overlapping of the lines by the lines or bands of foreign elements, this effect is shown up by a deviation of the galvanometer when the apparatus is adjusted to the lines of the test element for solutions of other salts introduced into the flame. Such interference was taken into account in our experiments.

2. The second type of interference and effect arises as a result of changes in the spraying or evaporating conditions of the drops, and also as a result of changes in the flame temperature. Poluektov et al.[33] on the basis of experimental results obtained with two atomizers are of the opinion that when working with solutions of alkali metal salts, the added alkali metal does not change the properties of the solution which affect the atomizing process, but rather mainly affect processes occuring in the flame. In our case the amount of solution containing 10 mg Rb/liter passing each second into the flame, with and without addition of 5000 mg KCL/liter, was almost the same.

The flame temperature only changes on introducing large concentrations of the alkali metal salts. Thus Tskhai and Mandel'shtam [34] have shown that the flame temperature starts to change on adding sodium at concentrations higher than 1 M; in our case the concentrations of NaCl and KCl added did not exceed 0.1 M.

3. One must take into account the effect connected with changes in the degree of dissociation of the molecules and the degree of ionization of the atoms of the test element in the presence of foreign elements. At the temperature of an air-acetylene flame the degree of dissociation at low concentrations of the alkali metals (partial pressure of the atoms n × 10^{-8} atm) will change very little on adding other alkali metals*. On the other hand, it is the change in the degree of ionization of the test element on adding to its solution another alkali element whose atoms themselves ionize and increase the concentration of free electrons in the flame, which is the main reason for the change in radiation intensity of test elements [13, 36-41].

We have calculated the change in the radiation intensity of Li, Na, Rb, and Cs on adding KCl and NaCl to solutions of their salts, on the assumption that these changes are solely the result of changes in the degree of ionization of the atoms of the test elements. The results obtained are in reasonably good agreement with experiment.

Calculations were carried out on the basis of the following formulas [13, 38, 39, 40, 41]:

$$\frac{p_1^+ p_e}{p_1} = K_1 \ldots (1); \quad P_1 = p_1 + p_1^+ \ldots. \qquad (2)$$

Since, in this case, when there are no foreign elements present in solution $p_1^+ = p_e$, equation (1) can be written in the following form [13]:

$$\frac{(p_1^+)^2}{p_1} = K_1$$

where p_1^+, p_1^- are the partial pressures of the ionized and neutral atoms of the test element; p_e is the partial pressure of the electrons; P_1 is the partial pressure of the total number of atoms of the test element, both ionized and unionized; K_1 is the ionization constant of the test element at a given temperature. The ionization constant was calculated by means of the formula:

$$\lg K = \frac{-5040\,U}{T} + 5/2 \lg T - 6{,}49, \qquad (3)$$

where T is the flame temperature in °K; U is the ionization potential of the test element in ev.

According to [13, 37, 42, 44] the temperature of an air-acetylene flame is 2530-2360°K. We adopted a value of 2430°K after correcting it so that the effect for Rb at a concentration of the latter of 10 mg/liter on adding 5000 mg KCl/liter, was close to the experimental value when all the remaining data were in good agreement with experiment. At this temperature the ionization constants were as follows:

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* Approximate calculations which we made on the basis of formulas taken from [3] for the degree of dissociation of Rb at a concentration of 10 mg/liter with and without addition of 5000 mg KCl/liter confirmed our assumptions. Formation of sparingly volatile and little dissociated compounds has only been observed for lithium, and not for the other alkali elements [11].

$$K_{\mathrm{Li}} = 6{,}22\cdot 10^{-10}$$

$$K_{\mathrm{Na}} = 2{,}11\cdot 10^{-9} \qquad K_{\mathrm{Rb}} = 2{,}06\cdot 10^{-7}$$

$$K_{\mathrm{K}} = 9.4\cdot 10^{-8} \qquad K_{\mathrm{Cs}} = 7\cdot 98\cdot 10^{-7}$$

For evaluating P we assumed that the experimental conditions we used were similar to those in [42, 43, and 44], in which the total number of atoms in 1 cm³ of the flame was considered to be given by

$$N_{\mathrm{total}} = 6.2 \times 10^{14} \text{ c atoms/cm}^3 \tag{4}$$

where c is the concentration of the salt in solution, M; from which

$$P_1 = \frac{6{,}2\cdot 10^{-14} c}{\frac{N_0}{V_0}\frac{273}{2430}} = 2\cdot 10^{-4}\, c \text{ atm}, \tag{5}$$

where N_0 is the Avogadro number, V_0 is the volume occupied by a mole of an ideal gas. For cases in which potassium and sodium salts were introduced into the solution, three equations were solved [13, 41]:

$$\frac{p_1^+ \cdot p_e}{p_1} = K_1 \ldots \tag{6}$$

$$\frac{p_2^+ \cdot p_e}{p_2} = K_2 \ldots \tag{7}$$

$$p_e = p_1^+ + p_2^+ \tag{8}$$

it is also borne in mind that

$$P_1 = p_1 + p_1^+ \tag{9}$$

$$P_2 = p_2 + p_2^+ \tag{10}$$

where P_1, p_1^+, and p_1 are the partial pressures of the total number of atoms, ionized, and neutral atoms of the test element respectively; P_2, p_2^+, and p_2 are the partial pressures of the total number of atoms, ionized, and neutral atoms of the influencing element; p_e is the partial electron pressure; K_1 and K_2 are the ionization constants of the test and influencing elements at a temperature of 2430°K.

The effect of the element introduced on the radiation intensity of the test element was calculated from the ratio of the number of its neutral atoms on adding KCl (or NaCl) to the number of neutral atoms for the case where no foreign elements are added, and also on the basis of the formula given in [30]:

$$I = CN(1 - X)e^{-E/KT}, \tag{11}$$

where X is the fraction of ionized atoms, C is a constant, N is the concentration of the element, and E is the excitation energy of the given line. The effect of the interference is given by:

$$\frac{i}{I_0} = \frac{1 - X}{1 - X_0}, \tag{12}$$

where X is the fraction of ionized atoms of the test element in the presence of the interfering element, and X_0 is the fraction of ionized atoms of the test element in the absence of any addition of interfering element.

The effects obtained experimentally and by calculation are compared in Tables 3-5.

Results of calculations show that the breakdown in the degree of ionization (Rb, Li, Na, Cs) which occurs on adding interfering elements KCl and NaCl can cause the effect which we have observed in our experiments.

It also follows from formula (5) that the effect of KCl on the radiation intensity of Rb, taken in equal amounts but in the form of different compounds, remains the same.

TABLE 3. Effect of 5000 mg KCl/liter on the Radiation Intensity of Li (670.8 $m\mu$), Na (589.3 $m\mu$), Rb (780.0 $m\mu$), and Cs (852.1 $m\mu$)

Test element, 10 mg/liter	5000 mg KCl/l introduced	
	I/I_0 experimentally determined	I/I_0 calculated
Li	0.99	1.0
Na	1.2	1.2
Rb	9.1	8.8
Cs	26.9	27.5

TABLE 4. Effect of the Same Amount of KCl and NaCl on the Radiation Intensity of Rb (780.0 $m\mu$) for Varying Contents of the Latter

Rb taken, mg/liter	5000 mg KCl/liter introduced		5000 mg NaCl/liter introduced	
	I/I_0 experimentally determined	I/I_0 calculated	I/I_0 experimentally determined	I/I_0 calculated
10	9.1	8.8	5.2	5.1
20	5.2	5.3	3.7	3.6
30	3.8	3.9	2.5	2.3
40	3.6	3.5	2.5	2.1

TABLE 5. Effect of Various Amounts of KCl and NaCl on the Radiation Intensity of Rb (780.0 $m\mu$) for a Constant Content of the Latter

KCl added, mg/liter	Test element Rb at a concentration of 10 mg/liter		NaCl* added, mg/liter	Test element Rb at a concentration of 10 mg/liter	
	I/I_0 experimentally determined	I/I_0 calculated		I/I_0 experimentally determined	I/I_0 calculated
5000	9.1	8.8	5000	5.2	5.1
500	6.1	6.4	500	2.8	2.7
50	2.6	2.8			

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* We did not calculate the effect of low concentrations of NaCl (50 mg/liter) on the radiation intensity of Rb, since calculations of the partial pressure of neutral Rb atoms in the presence of the interfering element was carried out approximately under conditions such that $p^+_{\text{interfering}}$ was considerably greater than p^+_{test}; at an NaCl concentration of 50 mg/liter they would be similar.

SUMMARY

The mutual effect of the alkali elements has been studied. It has been found that addition of potassium chloride at the rate of 5000 mg/liter to test solutions of the other alkali elements (at contents of 10 mg/liter) does not alter the radiation intensity of Li, slightly increases the radiation intensity of Na, while it increases the radiation intensity of Rb nine times and that of cesium 27 times. On increasing the concentration of the interfering element KCl from 50 to 5000 mg/liter, the radiation intensity of rubidium increases (for a rubidium concentration of 10 mg per liter); the radiation intensity increases 2.6 times on adding 50 mg KCl/liter, and 9.1 times on adding 5000 mg KCl/liter. At equal concentrations of the interfering element (KCl 5000 mg/liter) but varying concentrations of Rb (10, 20, 30, 40 mg/liter) the interference effect decreases as the Rb concentration increases; for 10 mg/liter it is 9.1 while for 40 mg Rb/liter it is 3.6.

The results obtained can, apparently, be explained by the change in the degree of ionization of the atoms of the test element on adding to its solution another alkali metal. Calculations which have been made are in good agreement with experimental and theoretical data.

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THE INFLUENCE OF CERTAIN ORGANIC MATERIALS ON THE RADIATION OF CALCIUM IN A FLAME IN THE PRESENCE OF ALUMINUM

E. E. Vainshtein and V. I. Lebedev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Weakening of the radiation intensity of calcium and strontium in the presence of a number of metals, in particular aluminum, is well known [1-3]. The magnitude of this effect depends on the concentration of the interfering elements in solution; it changes on switching from one test material to another, and on reaching a significant value leads to serious interference during flame photometric determination of the alkaline earth elements. As a result it is necessary (particularly during the analysis of rocks and minerals) to remove aluminum, iron, and other elements, or compensate for their influence on the experimental results artificially [4,5].

Recently Debras-Guedon and Voinovitch [6] showed that addition of 8-hydroxyquinoline to the test solution permits the influence of aluminum on the line intensity of calcium to be reduced appreciably. They made use of this fact for determining the alkaline earth elements without preliminary removal of aluminum. The significant practical importance of the effect discovered led us to carry out a more systematic study of the effect of various organic compounds (including 8-hydroxyquinoline) on the results of the flame photometric determination of calcium. In the course of this work, on the basis of the results of a series of researches, and, in particular on the results of experiments with two atomizers [7], which showed that aluminum depresses calcium radiation only when both metals are present in the same solution (and does not show such influence when these elements are introduced separately into the flame), it was possible to conclude that the basic reason for the "extinction" of the calcium radiation by aluminum is the formation in the aerosol, at the moment when it is evaporating, of a difficulty volatile compound (possibly $CaAl_2O_4$) which does not break down during passage through the flame. If this is the case, then weakening or complete elimination of the effect of aluminum on the line intensity of calcium can be achieved by one of two methods: either by ensuring conditions such that aluminum at the point when the aerosol evaporates, forms some stable compound, or leads to formation in the aerosol of a sufficiently stable compound of calcium which would, however, be relatively easily destroyed in the flame. It is obvious that in the latter instance, the most suitable components which form compounds that readily break down in the flame, would be organic materials.

On this basis, in the work described here, we studied the effect of acetylacetone, 8-hydroxyquinoline, and also oxalic and salicylic acids.

The instability constants [8] of the complexes are: for $Al[Ox]^{3-}-1.6\cdot10^{-17}$; and $AlSal^{3+}-8\cdot10^{-15}$ and $Al[Acac]_3$ $-5.0\cdot10^{-23}$. Nevertheless, the experimental conditions were such that the corresponding aluminum complexes were not, apparently, formed in solution. The values of the instability constants for the corresponding complex compounds of calcium are unknown in most cases.

Experiments were carried out with an acetylene-air burner of the Mekker type provided with a separate atomizing chamber. The section of the flame at a distance of 5 mm from the inner cones were measured photometrically. The spectral apparatus used was an ISP-51 spectrograph with a FÉP-1 photoelectric apparatus and a recording galvanometer.

Results illustrating the effect of additions of various amounts of organic materials on the radiation intensity of the resonance line Ca 422.7 mμ, for solutions containing different amounts of aluminum are shown in Figs. 1-3. In order to get a complete picture, curves characterizing the effect of additions of the organic material on the radiation intensity of calcium* in the absence of aluminum are given at the same time on each of the curves.

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* Experiments with strontium gave similar results.

Of great importance for clarifying the mechanism of the action of organic materials is the case of the effect of oxalate ions (Fig.1). Complexing of calcium ions by oxalate ions unfavorably affects the line intensity of calcium in the flame. The intensity gradually decreases with increasing oxalate ion concentration in solution. However, when the solution contains aluminum which is capable, under certain conditions, of forming more stable complexes with oxalate, in the presence of oxalate ions the calcium ions are prevented from forming a difficulty volatile chemical compound with aluminum, and under these conditions there is a significant increase in the intensity of the calcium spectral lines in the flame. While the oxalate concentration of the solution is still less than the equivalent concentration of aluminum, increases in the oxalate concentration promote complexing of increasing amounts of Al^{3+} ions and lead to a uniform increase in the line intensity of calcium (i.e., to a gradual and every increasing suppression of the "extinguishing" effect). When the oxalate concentration becomes equivalent to the aluminum concentration, the "extinguishing" effect of the latter on calcium reaches a minimum value, while the radiation intensity of calcium, correspondingly, becomes a maximum. Beyond this point there is observed a weakening in the line intensity of calcium caused by the "extinguishing" effect of the oxalate ion itself on calcium. The suggested mechanism which has been described for the action of oxalate ion on the "extinguishing" effect of aluminum with respect to the line emitted by calcium readily explains the shapes of all the curves given in Fig. 1. Since the maximum on these curves, in view of what has been said above, should be located near the equivalence point (denoted by dotted lines), this should enable one to get some idea of the composition of the complex formed in solution. According to our results, this complex has the formula $Al[C_2H_2O_4]^{3-}$ and is characterized [9] by an instability constant of 1.6×10^{-17}.

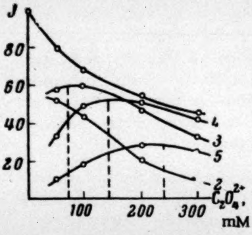

Fig. 1. Relationship between the intensity of the Ca line 422.7 and the concentration of oxalate ion for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 10 mM; 3) Al, 20 mM; 4) Al, 40 mM; 5) Al, 50 mM.

Considerably less definite results were obtained during a study of the effect of salicylic acid (Fig. 2). Despite the fact that salicylic acid itself (in contrast to the case considered previously) does not exhibit an "extinguishing" effect on the line intensity of calcium, a maximum is observed again in this case on all the curves, the position of which shifts forward higher molar concentrations of salicylic acid as the aluminum concentration of the solution increases. Possibly, this indicates formation of one or more less stable aluminum complexes in solution during passage of the latter through the flame when excess salicylic acid is present. In order to confirm this, however, one must, of course, have direct proof.

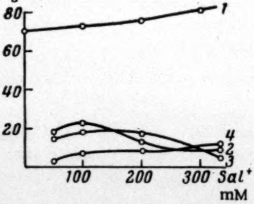

Fig. 2. Relationship between the intensity of the Ca line 422.7 and the concentration of salicylic acid for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 15 mM; 3) Al, 30 mM; 4) Al, 120 mM

The most interesting results from a practical point of view were obtained during a series of experiments with acetylacetone and 8-hydroxyquinoline (Fig. 3). The effect of these compounds on the radiation intensity of calcium in the presence of aluminum is approximately the same. In their presence (Fig. 3), in both cases, the maximum intensity of the calcium lines is considerably greater than in the presence of the other materials tested (Figs. 1-2).

The fact that in both cases no "extinguishing" effect on the calcium line is observed on adding these compounds, leads to a smooth increase in the line intensity of this element as the concentration of the acetylacetone or 8-hydroxyquinoline in solution increases. The greater steepness of curve "a" as compared with curve "b" in Fig. 3 is explained by the fact that in contrast to experiments with acetylacetone, in solutions containing 8-hydroxyquinoline the viscosity simultaneously increases considerably with increasing concentration of this compound.* This should lead, as a consequence, to a relative decrease in the line intensity of calcium for solutions with a higher content of the organic compound. As is evident, the effect of additions of organic compounds on the line intensity of calcium depends on the aluminum concentration of the solution, so that complete elimination of the "extinguishing" effect of aluminum, apart from its content, is, in general, not possible. We only observed such an effect in one instance when we introduced a 50% solution of acetylacetone in acetic acid (1:4) into the flame. Usually, however, in order to get correct results during determination of calcium in the presence of aluminum by the method indicated, one need only have an approximate idea of the aluminum content of the test solution. Matters are simplified during analysis of silicate rocks whose aluminum content does not usually exceed 20%. Without going into any details of the analytical technique, we should point out that on carrying out quantitative determination of calcium in rocks with the most diverse aluminum contents by means of calibration curves constructed with standards containing 0.25 mg aluminum/ml[*]; as our experiments have shown, the maximum experimental error will vary with the content of added organic compounds within the limits indicated in the cruves in Fig. 4. The experimental error in determining calcium following from the presence of an unknown amount of aluminum in the sample can, if required, be considerably decreased by using a large number of standard solutions, the aluminum concentration of which would correspond to its concentration in the test rocks.

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* Thus the viscosity of a 5% solution of 8-hydroxyquinoline is almost 1.5 times that of water. It should be emphasized that no precipitate of 8-hydroxyquinolate is formed under the experimental conditions used.

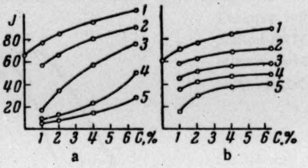

Fig. 3. The relationship between the intensity of the Ca line 422.7 and the concentration of acetylacetone (a) and 8-hydroxyquinoline (b) for different aluminum concentrations and a constant calcium content (25 mg/liter). 1) Al, 0 mM; 2) Al, 20 mM; 3) Al, 50 mM; 4) Al, 100 mM; 5) Al, 200 mM

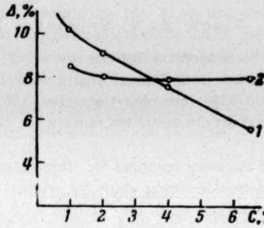

Fig. 4. The relationship between the value of the maximum experimental error in determining calcium, following upon a shift in the calibration curve in the presence of aluminum, and the concentration of 1) acetylacetone; 2) 8-hydroxyquinoline.

Results and conclusions similar to those made in the work described here with respect to aluminum and calcium, have also been obtained for other instances of "extinguishing" agents such as Ge, Ti and others, which, however, usually exhibit a much smaller influence on the flame photometric determination of the alkaline earth elements.

SUMMARY

A study has been made of the effect of a number of compounds capable of forming complexes with aluminum (oxalic acid, salicylic acid, 8-hydroxyquinoline, and acetylacetone) on the intensity of the spectral lines of calcium when the latter is determined by flame photometrically in the presence of aluminum. It has been shown that suppression of the "extinguishing" effect depends on the concentration of the organic compounds added, and on the aluminum content. A mechanism is suggested for the suppression of the "extinguishing" effect.

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[*] On the basis that a 250 mg aliquot dissolved in 100 ml it is used for determination of calcium and strontium.

PHOTOMETRIC DETERMINATION OF MAGNESIUM WITH THE REAGENT PICRAMINAZO

S. I. Gusev, E. V. Sokolova, and Z. A. Bitovt

Perm State Medical Institute

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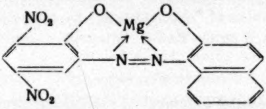
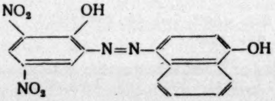
Most of the color reactions for magnesium are based on adsorption of various azo dyes and other materials by magnesium hydroxide during which the original color of the organic compound changes. In Kuznetsov's terminology [1] all these reactions are of the "colored solid phase" type. Azo- and diazo compounds having hydroxy- and nitro groups in the ortho or para positions with respect to the azo group are characteristic reagents for magnesium. Kul'berg [2] studied 25 azo dyes prepared by diazotization of p-nitroaniline. He has come to the conclusion that the change in the color of the dye during its interaction with magnesium ions in an alkaline medium is related to the development of an intracomplex compound. Kuznetsov showed that azo dyes with hydroxy and nitro groups in the ortho and para positions do not always give a color change with magnesium hydroxide. Moreover, there are a number of materials not containing the groups indicated, e.g. titanium yellow etc., which react with $Mg(OH)_2$. We completely share V. I. Kuznetsov's views regarding the mechanism of the interaction of magnesium with azo dyes and other materials in alkaline media, which is based on adsorption phenomena. We have examined azo dyes based on picramic acid; the molecular weight of these materials did not exceed 370-390. Without going into detail about all the experiments with azo dyes prepared for the first time, we should point out that on coupling diazotized picramic acid with α- and β-naphthols, compounds are formed which react with $Mg(OH)_2$ with an accompanying change in color. However, if Kul'berg's conclusions are correct [4], introduction of two hydroxy groups into the ortho position with respect to the azo group should sharply enhance the color of the reaction product as a result of the formation of an intracomplex compound;



this does not occur in actual practice. The azo dye obtained with β-hydroxynaphthol possesses low sensitivity to magnesium ions; on the other hand, coupling of diazotized picramic acid with α-naphthol gives a dye which permits detection of 0.25 μg Mg^{2+}/ml.

Below we give the results of a study of 2-hydroxy-3, 5-dinitro-1-azo-4, 1-hydroxynaphthalene (picraminazo)



as a potential reagent for magnesium during its determination in various materials, including biological materials. This reagent is a brown colored powder which is insoluble in acids and in cold water; it dissolves in ethanol, acetone, and caustic alkali solutions. The conditions used for determining magnesium by means of this reagent are similar to the conditions adopted for determination of magnesium by "phenazo" and titanium yellow. The caustic alkali concentration of the final solution is 1.5 N and higher. The absorption spectra of solutions of the reagent and of its compound with magnesium are shown in Fig. 1.

Picraminazo is readily synthesized and can be made in any laboratory.

Picraminazo permits determination of magnesium in the presence of up to 2000 times its amount of titanium in an alkaline solution, when the titanium is converted into peracid salts. Foreign ions which interfere are approximately those which interfere when previously suggested reagents are used. Interference from iron, manganese, zinc, and nickel cations can be eliminated by means of a solution of sodium diethyldithiocarbamate.

The sensitivity of the reaction with picraminazo for magnesium, according to Kuznetsov's microgram index [5,6] in extinction units is 0.022 at a wavelength of 580 mμ. This reagent therefore lies between phenazo and titanium yellow with respect to sensitivity [7]. F. M. and also FEK-M photometers can be used for magnesium determination by means of picraminazo, while the FÉK-M photometer cannot be used when the reagent adopted is magneson 1.

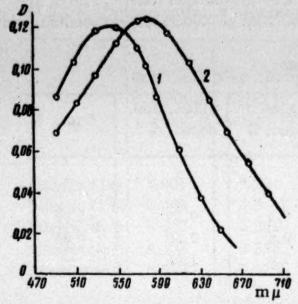


Fig. 1. Absorption of an alkaline solution of picraminazo (1) and with the magnesium hydroxide colored by it (2). Picraminazo solution 0.0000006 M; magnesium solution 0.00008 M; solution 1.8 N with respect to NaOH; path length of cell l = 20 mm.

A 0.005% ethanol solution of reagent was used for the photometric determination of magnesium. The solution can be stored without change for several months.

EXPERIMENTAL

Synthesis of Picraminazo Reagent. Five g of picramic acid was dissolved in 200 ml ethanol; hydrochloric acid (15 ml HCl sp.gr. 1.19 and 15 ml water) was then added to the solution. The mixture was cooled in ice. The calculated amount of 10% sodium nitrite solution was added slowly with careful stirring to the cooled solution. After 30 min the crystalline precipitate which had separated out was sucked off on a Buchner funnel; the precipitate was washed with a small amount of ice water, it was then transferred to a beaker and suspended in 50 ml of water. Twenty ml of a 10% ethanol solution of α-naphthol was added to the pasty mass. The mixture started to darken immediately and a dark-red color developed. To this mixture was added 10 ml of a saturated solution of Na_2CO_3. Fifty ml of acetic acid was added dropwise with stirring over a period of 3 hours and this was followed by 10 ml HCl (sp.gr. 1.19). The dye formed was heated on a boiling water bath, it was then filtered off and washed with a small amount of hot water. The material obtained was suspended in 500 ml of water, sodium hydroxide was added, and the solution obtained filtered free from insoluble residue; by acidifying the filtrate with hydrochloric acid the pure dye was separated out, the dye was then washed until the washing gave no reaction for chloride ion, and was finally dried at room temperature. A brick colored product was obtained; yield about 8 g.

Determination of Magnesium in Alloys

a) Cast Iron. An aliquot (about 1 g) of cast iron was dissolved on heating in hydrochloric acid (sp.gr. 1.19). The solution obtained was transferred to a 100 ml standard flask, diluted with water to the mark and the whole mixed. Ten ml of this solution was transferred to a 100 ml flask and neutralized with sodium hydroxide solution until the solution gave a blue-violet color with congo red paper; 20 ml of a 10% sodium diethyldithiocarbamate* solution was then added, the volume of the solution was made up to the mark with water and mixed. Part of the solution was filtered through a fine dry ashless filter paper into a dry flask. Ten ml of the filtrate was transferred to a 50 ml standard flask, 5 ml of 0.5% gelatin solution, 2 ml of 0.005% reagent solution, and 15 ml of 20% sodium hydroxide were added and the volume of the solution made up to the mark with water; the whole was mixed and the optical density measured on a FÉK-M photoelectric colorimeter using a red filter and a cuvette with l = 50 ml. Standard solution: 2 ml of 0.005% reagent solution, 5 ml of 0.05% gelatin solution, 15 ml of 20% sodium hydroxide solution, water to the mark in a 50 ml standard flask. Results of determinations are given in Table 1.

b) Titanium Alloys. An aliquot of alloy (1 g) was dissolved by Kuznetsov's method by heating it in 70 ml of hydrochloric acid (sp.gr. 1.19). The solution obtained was transferred to a 100 ml standard flask, diluted with water to the mark and mixed. A ten ml aliquot of this solution was pipetted into another standard flask (100 ml) and 20% sodium hydroxide solution added until the solution gave a blue-violet color with congo red paper. To the solution obtained after adding sodium hydroxide was added 20 ml of a 10% solution of sodium diethyldithiocarbamate and the solution diluted with water to the mark. Part of the solution was filtered through a fine dry filter paper. Ten ml of the filtrate was transferred to a 50 ml standard flask and the procedure outline above for cast iron analysis then followed.

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* When this work was complete a short communication appeared in Zavodsk. laboratoriya, 21, No. 11 (1960) relating to the determination of magnesium in cast iron, in which the elements which interfere with this determination were precipitated beforehand with sodium diethyldithiocarbamate.

During determination of magnesium in undegassed and degassed titanium, after the aliquot of titanium has been dissolved in hydrochloric acid, and the solution has been diluted with water until the total volume of the solution in the standard flask was 100 ml, 10 ml of the solution was transferred to a 50 ml standard flask; 0.5 ml of hydrogen peroxide, 5 ml of a freshly prepared and filtered 0.5% solution of starch, 2 ml of 0.005% reagent solution, and 15 ml of 20% sodium hydroxide solution were added; the solution obtained was diluted to the mark with water. The optical density was measured after 10-15 min. The standard solution was prepared in the same way as that described for analysis of cast iron, the gelatin solution being replaced by starch solution. Results of determinations are given in Table 2.

TABLE 1. Determination of Magnesium in Iron Alloys by Means of Picraminazo

Alloy	Magnesium added, %	Magnesium found, %	Error, %	Alloy	Magnesium added, %	Magnesium found, %	Error, %
Magnesium free cast iron				Magnesium free cast iron			
No. 191	1.22	1.22	–	No. 193	0.3	0.32	+0.02
No. 191	1.22	1.19	-0.03	No. 193	0.6	0.58	-0.02
No. 192	1.00	1.00	–	No. 193	1.0	1.00	–
No. 192	1.00	1.00	–				

TABLE 2. Determination of Magnesium in Titanium and Its Alloys

Test material	Magnesium content, %	Magnesium added, %	Magnesium found, %
Chemically pure titanium	–	0.5	0.50; 0.49; 0.51; 0.51
Undegassed titanium	0.47	–	0.47; 0.47
Undegassed titanium	0.47	0.5	0.96; 0.97; 0.95
Alloys based on titanium		0.2	0.2; 0.2; 0.19; 0.21; 0.51;
(VTZ-1)		0.5	0.50

c) Aluminum Alloys. An aliquot of alloy (0.2 g) was dissolved by V. I. Kuznetsov's method in 20 ml of 20% sodium hydroxide solution, the solution obtained was diluted with water to 150-200 ml and filtered through a fine paper, and the precipitated washed several times with 2% sodium hydroxide solution. The precipitate was dissolved on the filter with 10-12 ml of hydrochloric acid (sp.gr. 1.19), the solution being passed into a 100 ml standard flask. The filter was washed several times with hot water. The solution obtained was neutralized with sodium hydroxide until it gave a blue-violet color with congo red paper. Fifteen ml of 5% sodium diethyldithiocarbamate solution was added and the solution diluted with water to the mark. Ten ml of solution which had been filtered through a fine filter paper was transferred to a 50 ml flask. The analytical procedure that followed was the same as that for analysis of cast iron. Results are given in Table 3.

Determination of Magnesium in Water. 5-10 ml of water (depending on the expected magnesium contact) was pipetted into a 50 ml standard flask, 2 ml of 0.005% reagent solution, 5 ml of 0.5% gelatin solution, and 15 ml of 20% sodium hydroxide solution were added, and the volume of the solution made up to the mark; the whole was mixed. The optical density was measured after 10-15 min. Results for analysis of mineral waters are given in Table 4.

Determination of Magnesium in Biological Materials. 0.1-0.2 g of dried biological material (muscle, liver, spleen, etc.) was wet oxidized by the usual method in a Kjeldahl flask with sulfuric acid and hydrogen peroxide.

After complete break down, the solution was quantitatively transferred to a quartz basin and excess acid removed by evaporation. The residue was transferred to a 100 ml standard flask and neutralized with sodium hydroxide until the solution gave a blue-violet color with congo red paper. Twenty ml of 1% sodium diethyldithiocarbamate solution was added and the solution diluted to the mark with water and mixed. Part of the solution was filtered through a dry filter paper and 10-20 ml of the solution taken for analysis. The procedure described for analysis of cast iron was then followed. Results for air-dry materials are given in Table 5.

TABLE 3. Determination of Magnesium in Aluminum Alloys by Means of Picraminazo

Alloy	Specified magnesium content, %	Magnesium added to sample, %	Amount of magnesium that should be present, %	Magnesium found, %	Alloy	Specified magnesium content, %	Magnesium added to sample, %	Amount of magnesium that should be present, %	Magnesium found, %
Silumin 113a	0.065	0.25	0.315	0.315	Silumin No. 4	–	0.25	0.25	0.25
Silumin 113a	0.065	0.5	0.565	0.575	Silumin No. 4	–	0.5	0.5	0.5
Silumin No.3	0.035	0.25	0.285	0.285	Dural No.69-σ	0.67	–	–	0.68
Silumin No.3	0.035	0.375	0.41	0.385	Dural No.69-σ	0.67	–	–	0.69
Silumin No.3	0.035	0.500	0.535	0.535					

TABLE 4. Determination of Magnesium in Mineral Waters by Means of Picraminazo

Water	Specified magnesium content, mg/liter	Magnesium found by means of picraminazo	Water	Specified magnesium content, mg/liter	Magnesium found by means of picraminazo
Slavyanovskii	43.7	44	Smirnovskii	40.1	42.2
Bitautas	226	230	Batalovskii	1533	1500
Essentuki No. 20	89.1	88	Narzan	110	108
Izhev source	186	190			

TABLE 5. Determination of Magnesium in Biological Materials (White Rat)

Test material	Aliquot, g	Magnesium added, mg, %	Magnesium found, mg, %	Magnesium that should be present, mg, %	Deviation, mg, %
Spleen	0.1986	–	144.8	–	–
Spleen	0.2002	50	193.8	194.8	-1.3
Blood clots	0.0918	–	103.5	–	–
Blood clots	0.0922	40	140.9	143.9	-2.6
Liver	0.1900	–	92.1	–	–
Liver	0.1986	50	142.3	142.1	+0.2

SUMMARY

A new reagent for magnesium called picraminazo has been synthesized. The reagent possesses a high sensitivity.

Photometric methods have been developed for determination of magnesium in cast iron, titanium and its alloys, alloys based on aluminum, mineral water, and biological materials. All the methods are reasonably simple and accurate and take comparatively little time.

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PHOTOMETRIC DETERMINATION OF THE CALCIUM CONTENT OF CEMENT MATERIALS BY MEANS OF COMPLEXONS

I. V. Bogdanova

State All-Union Scientific-Research Institute of the Cement Industry, Leningrad

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Photometric methods of determining SiO_2, Al_2O_3, and Fe_2O_3 [1] in raw materials and finished products are widely used in many cement plants. It would be expedient to develop a photometric method for the determination of CaO, particularly since visual complexometric titration of calcium is complicated by the fact that the color change of the indicator at the end point is not clear enough.

There is very little information on photometric methods of determining calcium. Thus Sandell [2] recommends two indirect methods for the photometric determination of calcium after it has been precipitated. Marti et al. [3] have determined microamounts of calcium on the basis of the weakening of the color of an iron salicylate solution by sodium oxalate remaining in excess after precipitation of calcium ions. A method exists which is based on decolorization of chloranilic acid by calcium salts [4]. The method requires removal of the precipitate of calcium chloranilate and uses a reagent which is not readily available. Murexide has been used in some papers [5,6] for photometric determination of calcium. Nevertheless, the dye is not very stable (not more than 8 hr) even in ethanolic solution, and the optical density of the solutions must be measured within 5 min. In addition, iron, manganese, cobalt, and certain other ions interfere with the determination when they are present in solution.

Calcium [7] which was recently synthesized both for the titrimetric and photometric determination of calcium has some essential drawbacks: the experimental results depend to a large measure on the salt concentration of the solutions which are being photometrically measured; this excludes the possibility of using this reagent for the analysis of cement materials.

All the methods outlined above are applicable for the determination of not more than 5-10% Ca, whereas the calcium content of cement materials amounts to 40-70%.

As the foundation of the method which we should like to suggest for the determination of high contents (40-45% Ca) we set a method based on complexing most of the calcium as a colorless complex and obtaining a colored compound with the remaining free calcium ions (amounting to 5-6%). This allows the accuracy with which calcium is determined to be increased by one order. Such a method is suitable for series of samples, in which the concentration of the test element varies within the limits 5-6%. Thus during determination of calcium in raw mixes it is possible to complex 40% of it into a stable complex with sodium ethylenediaminetetracetate (EDTA-Na), so that only the remaining 2-5% of the calcium ions will participate in formation of the colored compound. This is possible because the instability constant of calcium ethylenediamietetracetate is significantly less than with metallo indicators. As a result it is possible to attain an absolute error of 0.2-0.3% for such amounts of calcium.

Formation of a compound between calcium ions and acid chrome dark-blue was chosen for the photometric determination of calcium. Aqueous solutions of acid chrome-dark-blue are stable for several weeks. We had to abandon the use of murexide because of the insufficient stability of even its ethanolic solutions. Eriochrome black T is also unstable in the presence of masked sesquioxides.

In studying the conditions for the formation of the colored compound of calcium with acid chrome dark-blue in pure solutions of calcium, and in the presence of other cations, it was necessary to follow the character of the absorption of light by these solutions, to establish the optimum concentration of the dye, alkali, EDTA-Na, and triethanolamine, and to check on the absence of interference on the part of magnesium, iron, and aluminum.

The preliminary experiments and construction of calibration curves were carried out with pure solutions of $CaCl_2$ in 0.5 N HCl containing 0.12 mg CaO/ml, corresponding to a content of 2% CaO in the samples on taking an aliquot of 0.15 g, diluting to 500 ml, and taking a 20 ml aliquot of the solution.

In the presence of calcium ions, acid chrome dark-blue has a red color, while in their absence the color is violet-blue. The sensitivity of acid chrome dark-blue for calcium ions at pH 9-13 is 1.4×10^{-7}g/ml, while for magnesium ions the sensitivity of this dye is 2×10^{-8}g/ml.

To attain the highest concentration sensitivity it is necessary to choose definite wavelength for measuring the optical density of the solutions. In order to do this we studied the absorption curves of a 0.02% aqueous solution of the free reagent in the presence of 1.7 mg of calcium completely complexed with EDTA-Na, and of solutions containing the reagent uncomplexed calcium ions in amounts of 100 and 275 μg in excess of the amount of calcium given above. The conditions used for obtaining the colored solutions are given below.

As Fig. 1 shows, the largest difference in optical densities corresponds to a wavelength of 600 mμ; i.e., measurement of the optical density of the solutions must be carried out with a yellow filter (λ_{max}= 595 mμ), and on the basis of the weakening of the dye color. Ten ml of a 0.02% aqueous solution of the reagent is added; under these conditions the change in optical density occurs in the most favorable part of the scale of the apparatus for experimental work, and a sufficiently high accuracy is ensured.

Calcium is determined photometrically in a strongly alkaline medium at pH ≥12; under such conditions magnesium is precipitated as its hydroxide and does not react with acid chrome dark-blue the residual magnesium concentration is 10^{-11}g/ml which is significantly lower than the sensitivity of the reagent for magnesium. As a result it is possible to determine calcium in the presence of magnesium when the pH of the solution has the appropriate value [8].

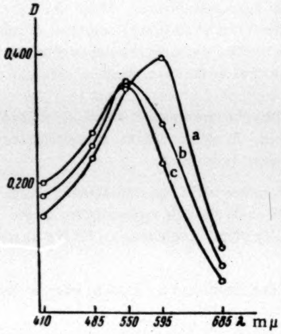

Fig. 1. Absorption curves of solutions of acid chrome dark-blue (a), and of solutions of its complexes with various amounts of calcium: b) 100 μg; c) 275 μg.

The optimum concentration and the amount of alkali added were established by examining the effect of various amounts of NaOH on the position and nature of the calibration curves for pure solutions of calcium.

A calibration curve was constructed by introducing 20 to 23 ml of standard $CaCl_2$ solution at 0.5 ml intervals into 100 ml standard flasks; these amounts of standard solution corresponded to CaO concentrations in the raw mixes of 40 to 46% in 1% intervals. Twenty ml of 0.00450 M EDTA-Na solution was then added to each flask; this complexed the same amount of calcium (about 40%) into a stable colorless complex. The solutions were made alkaline with 5 ml of NaOH of the following concentrations: 5, 10, 15, and 30%. Ten ml of dye solution was added, and the volumes made up to the mark with water. The optical density of the solutions obtained was measured on a FEK-M apparatus using a 10 mm cell and a yellow filter. The color of the solution is stable for 30 min. The calibration curves (Fig. 2) confirm the reversibility of the complex forming reaction: with increasing CaO and NaOH concentration there is a shift in the equilibrium as a result of which the lines become curves and the Lambert-Beer law is no longer obeyed.

In addition, increases in the alkalinity lower the slope of the curves and lead to a decrease in sensitivity. Five ml of a 10% NaOH solution can be regarded as the optimum amount. Further decreases in alkalinity significantly increase the dependence of the optical density on variations in pH.

A 1% aqueous solution of triethanolamine (TEA) for masking iron and aluminum was used during a study of the effect of magnesium, aluminum, and iron on the results of calcium determination. More complete and stable masking of aluminum was realized by introducing 0.5% sodium fluoride into the TEA solution. Five ml of the prepared mixture was added. At the same time we examined the effect of standing the test solutions for 10 min after addition of 5 ml of alkali to them.

On the basis of the results obtained (Table 1) it can be concluded that during analysis of samples containing up to 5% MgO and 10% Al_2O_3 one need not leave the solutions to stand. In the case of samples with a higher magnesium content the alkali solutions must be allowed to stand for 10 min for preliminary formation of a magnesium precipitate. Sodium fluoride must be added whatever conditions are used.

We were unable to eliminate interference when 0.36 mg of magnesium and 0.63 mg of aluminum were present in 100 ml of the final solution. Iron, even in amounts of 1 mg, did not interfere with calcium determination.

Since the content of calcium and sesquioxides in cement materials is considerably lower than the established limits, there is no interference from the sesquioxides during photometric determination of calcium (Table 2).

The mean square error is 0.1%.

The analytical conditions used were as follows. A 0.15 g aliquot of sample was fused with 1 g of fusion mixture (one part borax, two parts soda). The melt was dissolved on continuous stirring in 100 ml HCl (1:3) and the solution transferred to a 500 ml standard flask; the volume of the solution was then made up to the mark with water. After mixing, a 20 ml aliquot was transferred into a 100 ml standard flask, and 5 ml of the mixture of 1% TEA solution containing 0.5% NaF added; this was followed by 20 ml of 0.00450 M EDTA-Na solution. The solution was next neutralized with 10% NaOH using methyl red as indicator and an excess of 5 ml of alkali was then added. After addition of 10 ml of dye solution, the volume was made up to the mark with water. The mixed solution was measured photometrically. The percentage content of CaO was determined on the basis of the extinction value.

TABLE 1. Effect of Magnesium, Iron, and Aluminum on the Results of Calcium Determination

Experimental conditions	Absolute systematic error (%) in the determination of the percentage content of CaO in the presence of:									
	MgO, %				Fe_2O_3, %		Al_2O_3, %			
	5	8	10	15	15	20	5	10	15	20
Without NaF, and without allowing to stand	+0,65	+1,05	—	—	0,0	–0,10	+0,55	+2,0	+2,82	—
Allowed to stand for 10 min	0,0	+0,30	+0,60	+0,90	–0,15	+0,09	–0,22	+0,18	+0,44	+0,70
With NaF, and without allowing to stand	+0,25	+0,75	—	—	0,0	+0,18	0,0	+0,14	+0,22	+0,38
Allowed to stand for 10 min	0,0	+0,05	+0,40	+0,55	–0,03	+0,05	+0,06	–0,12	–0,20	–0,34

TABLE 2. Comparative Results for the Photometric and Titrimetric Methods of Determining CaO in Cement Materials

Sample	CaO content, %					
	titrimetric method	photometric method				deviation (absolute), %
Standard raw mix	42.70	42.67	42.74	42.81	42.74	+0.04
Leningrad plant raw mix	43.26	43.20	43.24	43.13	43.19	-0.07
Spasskii plant raw mix	44.65	44.89	44.72	44.72	44.78	+0.13
Rizhskii plant raw mix	43.45	43.39	43.28	43.37	43.38	-0.07
Pikalevskii plant clinker	61.30	61.26	60.96	61.38	61.20	-0.10
Bryanskii plant clinker	66.28	66.02	66.20	66.08	66.10	-0.1
Volkhovskii plant clinker	65.45	65.59	65.49	65.26	65.45	0.08
Irkutsk plant clinker	63.31	63.25	63.49	63.33	63.38	+0.08

At the same time a solution of a standard raw mix with a known CaO content, as determined by several methods, was examined, with the aim of introducing corrections for changes in the photometric conditions from those used for constructing the calibration curve; the changes are usually accompanied by parallel displacements of the calibration curve. This was carried out as follows: when, under the new conditions, but using a calibration curve constructed earlier, we found a CaO content in the standard raw mix which was, e.g., 0.3% higher than it should be, this value was subtracted from the CaO content found for the test sample, while if the CaO content was 0.3% lower, then this value was added.

Analysis of samples of raw mixes and clinkers was carried out using the same calibration curve. Only 0.1 g of clinker was taken for analysis; results of the determinations increased 1.5 times. A concentration range of 61 to 67% was covered.

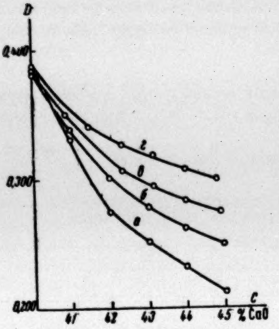

Fig. 2. Effect of the alkalinity of calcium solutions on the position and the nature of the calibration curves on adding NaOH of the following concentrations: a) 5%; b) 10%; c) 15%; d) 30%.

During clinker analysis corrections were initially applied, subsequently the results were multiplied by 1.5.

Determination of CaO, without taking into account fusion and dissolution, takes about 15 min.

Chemically pure or analytical grade calcium carbonate or standard sample of raw mix can be used for constructing the calibration curve; these materials should be taken through all the same analytical operations as the test samples.

SUMMARY

A photometric method is suggested for the determination of high concentrations of calcium which does not involve separation of sesquioxides; the method is based on complexing most of the test calcium with EDTA-Na into a colorless complex and on formation of a colored compound with the remaining free calcium ions. The error does not exceed ≠0.3% (absolute) for calcium contents in cement mixtures ranging from 40 to 45%, and in clinkers from 60 to 67%. A single determination, excluding fusion and dissolution of sample, takes about 15 min.

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DETERMINATION OF CERIUM IN CAST IRON BY TITRATION WITH HYDROQUINONE SOLUTION

A. A. Amsheeva and D. V. Bezuglyi

Khar'kov Polytechnical Institute and the V. A. Malyshev Transport
Machinery Construction Plant

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We have developed a reliable and comparatively rapid method for determining cerium in ferrous metals. It consists of: a) separating cerium as its fluoride from other elements at pH 2-5; b) rapid and accurate titrimetric determination of cerium with hydroquinone solution.

It is often recommended that the main element be removed by electrolysis with a mercury cathode [1]; this method, however, is not very convenient for plant laboratories; precipitation of cerium as its periodate [2], oxalate [3], and iodate is not applicable to the analysis of cast iron. The solubility product of CeF_3 as determined radiometrically is 8.1×10^{-16}, while the value determined conductometrically is 1.1×10^{-15} [4]. According to the results of the same authors the solubility of cerium fluoride depends on the pH of the solution, thus at pH 2 it is equal to 3×10^{-5} M, while at pH 1 it is 1.2×10^{-4}M, and at pH 0 it is 1.1×10^{-3} M. Ferric ions should be absent, since they bind fluoride ions into a stable complex, while in the presence of ferrous iron a precipitate of $FeF_2.FeF_3$ [5] is given; accordingly, before precipitating the CeF_3, ascorbic acid is added to the solution to prevent oxidation of ferrous iron.

The precipitate of the fluorides is filtered off, washed, and after ashing, treated with sulfuric acid to remove HF completely; in this way a solution of the sulfate of the rare earth elements is obtained which is almost free from impurities. An aliquot of cast iron containing 2-3 mg of cerium is taken and it is best to determine such an amount titrimetrically. Volodarskaya [6] recommends that cerium be oxidized to its quadrivalent state by ammonium persulfate (without using silver nitrate) and that titration be carried out with 0.02 N ferrous sulfate in the presence of ferroin. A hydroquinone solution, however, possesses appreciable advantages as a reducing agent [7]. Although the redox potential of the system hydroquinone–quinone (0.681 v) is higher than that of other systems (ascorbic acid, +0.43 v; stannous chloride, +0.2 v), hydroquinone is convenient in that at normal temperature, in acid solution, it immediately and quantitatively reduces quadrivalent cerium, and also iodide, bromide, chloride, bromate, chromate, and vanadate. A solution of hydroquinone in 1-3% sulfuric acid is stable on storage.

Ferroin or diphenylamine can be used as indicators but the former is preferable.

Cerium can be determined with reasonable accuracy in the presence of lanthanum, neodymium, and praseodymium by means of hydroquinone. Trivalent iron and sexivalent molybdenum do not interfere at contents less than 5 mg; at higher contents of these ions positive errors are obtained. Vanadates and chromates also interfere.

Determination of Cerium in Synthetic Mixtures. Cerium sulfate solution was standardized gravimetrically using the oxalate method.

The solution of hydroquinone (0.005 N) in 1% sulfuric acid was standardized against ceric sulfate solution.

A 0.025 M solution of indicator, o-phenanthroline–ferrous sulfate (ferroin), was used.

150 ml of water was added to 10 ml of cerium sulfate solution contained in a 250 ml flask, 5 ml of sulfuric acid sp.gr. 1.84 was added and the cerium oxidized with 25% ammonium persulfate solution. After oxidation, the solution was boiled for 5-7 min (until excess oxidizing agent had been completely destroyed) and then cooled. The quadrivalent cerium in the cooled solution was titrated with 0.005 M hydroquinone, after addition of one drop of ferroin, until a rose color appeared.

Experiment No. 1. Ten ml of cerium salt solution was taken ($T_{Ce} = 0.000400$ g/ml). Titration results and their statistical treatment are given in Table 1.

$\overline{x} = 4.000 - \frac{1.1 \cdot 10^{-1}}{7} = 4.000 - 0.016 = 3.984$: $\Sigma (x_i - \overline{x})^2 = 4.3 \cdot 10^{-3} - 7 \cdot (4.000 - 3.984)^2 = 4.3 \cdot 10^{-3} - 7 \cdot (0.016)^2$ $= 2.5 \cdot 10^{-3}$; $S^2 = \frac{2.5 \cdot 10^{-3}}{6} = 0.41 \cdot 10^{-3}$; $S_x = \frac{2.5 \cdot 10^{-3}}{7.6} = 7.7 \cdot 10^{-3}$; $= t_1 = \frac{4.000 - 3.984}{7.7 \cdot 10^{-3}} = \frac{16 \cdot 10^{-3}}{7.7 \cdot 10^{-3}} = 2.1$

which gives a reliability of $\alpha = 0.93$.

TABLE 1.

x_i, mg	$(x_i-4) \cdot 10^3$	$(x_i-4)^2 \cdot 10^4$
4,00	0	0
4,00	0	0
4,00	0	0
3,97	—3	9
3,95	—5	25
3,97	—3	9
4,00	0	0
Total	$-1,1 \cdot 10^{-1}$	$4,3 \cdot 10^{-3}$

It is possible to say therefore with a probability of 0.93 that the accuracy which can be reached for cerium determination is $\pm 2.1 \cdot 7.7 \cdot 10^{-3}$ $= \pm 15.7 \cdot 10^{-3}$ mg, or 0.4% (relative).

Experiment No. 2. Ten ml of cerium salt solution taken ($T_{Ce} = 0.000171$ g/ml).

Five determinations were carried out.

Results of statistical treatment are as follows:

$$\overline{x} = 1,7\ \ 7 \text{ mg};\quad \Sigma (x_i - x)^2 = 0,8 \cdot 10^{-4};$$

$$S^2 = \frac{0,8 \cdot 10^{-4}}{4} = 0,2 \cdot 10^{-4};\quad S_x = \sqrt{\frac{0.8 \cdot 10^{-4}}{4 \cdot 5}} = 2 \cdot 10^{-3};$$

$$t_1 = \frac{1,717 - 1,710}{2 \cdot 10^{-3}} = 3,5;\quad \alpha = 0,97.$$

The experimental accuracy is: $\pm 2 \cdot 10^{-3} \cdot 3.5 = \pm 7 \cdot 10^{-3}$ mg, or 0.4% (relative).

Experimental No. 3. Ten determinations of cerium were carried out in solutions with increasing cerium contents from 0.6 to 15 mg.

The statistical treatment of the results is given in Table 2.

TABLE 2.

Ce taken x_1, mg	0,60	1,200	1,710	1,800	2,400	3,000	4,000	6,000	9,000	15,000
Ce found y_1, mg	0,598	1,199	1,717	1,788	2,395	2,974	3,984	6,017	9,040	14,980
$\frac{y_i}{x_i} = z_i$	0,9866	0,9991	1,0041	0,9933	0,9980	0,9913	0,9960	1,0026	1,0044	0,9987
$(z_i - \overline{z}) \cdot 10^3$	—10,8	+1,7	+6,7	—4,1	0,60	—6,1	—1,4	+5,5	+6,8	+1,330
$(z_i - \overline{z})^2 \cdot 10^5$	11,66	0,289	4,489	1,681	0,036	3,721	0,196	2,916	4,624	0,169

The following values were calculated from the results given in this table.

$\Sigma z_i = 9,9743$ $\overline{x} = 4,471$
$\Sigma x_i = 44,71$ $\overline{y} = 4,468$
$\Sigma y_i = 44,681$ $\overline{z} = 0,9974$
$\Sigma x_i y_i = 380,670$ $\Sigma (x_i - \overline{x})^2 - 180,028$
$\Sigma (x_i)^2 = 380,72$ $\Sigma (z_i = \overline{z})^2 = 3,005 \cdot 10^{-4}$
$\Sigma (y_i)^2 - 380,484$

The relation between the amount of cerium taken and that found is expressed by the equation for a straight line:

$$y = a + bx$$

where a is the value of the intercept on the ordinate and b characterizes the slope of the line to the abscissa.

The coefficients are calculated as follows [8, 9]:

$$b = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma y_i}{n\Sigma (x_i)^2 - (\Sigma x)^2} = \frac{10 \cdot 380,670 - 44,71 \cdot 44,681}{10 \cdot 380,72 - (44,71)^2} = 0,9993;$$

$$a = \bar{y} - b\bar{x} = \frac{\Sigma y_i - b\Sigma x_i}{n} \frac{44,681 - 0,9993 \cdot 44,71}{10} = 0,0003.$$

Thus the relation between x and y is expressed by the equation for a straight line in the form

$$y = 0.9993x + 0.0003$$

$Y_{calc.}$, $y_i - Y_{calc.}$, $(y_i - Y_{calc.})^2$ and $\Sigma (y_i - Y_{calc.})^2$ are calculated by means of this equation. These values are given in Table 3.

TABLE 3.

$Y_{calc.}$	0,5999	1,199	1,698	1,799	2,399	2,998	3,997	5,996	8,994	14,990
$y_i - Y_{calc} \cdot 10^3$	7,9	0	12	—11	—4	—24	—13	21	46	—10
$(y_i - Y_{calc})^2 \cdot 10^5$	6,2	0	14,4	12,1	1,6	57,6	16,9	44,1	212,6	10

From which $\Sigma(y_i - Y_{calc.})^2 = 3.68 \times 10^{-3}$;

$$S_y = \sqrt{\frac{\Sigma (y_i - Y_{calc})^2}{n-2}} = \sqrt{\frac{3,68 \cdot 10^{-3}}{8}} = 2,2 \cdot 10^{-2};$$

$$S \left(\text{from the ratio } \frac{y_i}{x_i}\right) = \sqrt{\frac{3,005 \cdot 10^{-4}}{9}} = 0,6 \; 10^{-2};$$

$$Sa = S \sqrt{\frac{\Sigma x_i^2}{n\Sigma x_i^2 - (\Sigma x_i)^2}} = S \sqrt{\frac{380,72}{10 \cdot 380,72 - (44,71)^2}} =$$

$$= 0,6 \cdot 10^{-2} \cdot 0,46 = 0,27 \cdot 10^{-2}; \; Sa = 0,27 \cdot 10^{-2}.$$

$$Sb = \frac{S}{\Sigma x_i^2 - \bar{x}\Sigma x_i} = \frac{0,6 \cdot 10^{-2}}{\sqrt{380 \cdot 72 - 4,471 \cdot 44,71}} = \frac{0,6 \cdot 10^{-2}}{13,42} = 0,45 \cdot 10^{-3}; \; Sb = 0,45 \cdot 10^{-3}.$$

Results of the statistical treatment show that the straight line expressing the relationship between the amount of cerium taken and that found by our method, passes through the origin, i.e., there is no systematic error.

The slope found for the straight line (0.9993) is in good agreement with z (0.9974), accordingly, the suggested method possesses adequate precision.

Determination of Cerium in Cast Iron. A 1-3 g aliquot of cast iron (depending on the cerium content) is introduced into a 250 conical flask; 25-30 ml of HCl (1:1) is added and the whole heated until the aliquot has dissolved completely. The solution is filtered free from graphite into a 100 ml conical flask. The volume of filtrate plus washing should not exceed 50 ml. 0.5 g of ascorbic acid is added to the cold solution to reduce trivalent iron, and 25% ammonia solution added dropwise to incipient precipitate formation. 0.5 g of sodium fluoride is added, and, after the flask has been sealed with a tight fitting rubber stopper, its contents are vigorously shaken for one hour (mechanical shaking).

The precipitate of fluorides are filtered off on a fine filter and washed 4-5 times with hot water. Filter plus precipitate are placed in a porcelain crucible; they are ignited and calcined gently in a muffle at not too high a temperature.

The calcined residue is transferred from the crucible into a 250 ml flask. 15 ml of sulfuric acid (1:4) is added and the liquid evaporated to the appearance of thick white fumes of SO_3 in order to remove fluoride completely. The cooled residue is dissolved in 150 ml of water, a further 5 ml of sulfuric acid sp.gr. 1.84 is added and the cerium oxidized with 10-25 ml of 25% ammonium persulfate. The whole is boiled for 5-7 min for complete removal of excess oxidizing agent. One drop of ferroin solution is added to the cooled solution and titration carried out with 0.005 N hydroquinone solution to the appearance of a rose color.

We have adopted this method in our laboratory for analyzing modified cast iron.

Results of the analysis of three samples of cast iron are given to characterize the method (Tables 4 and 5):

TABLE 4.

Sample no.	% Cerium according to each determination					
1	0,0538	0,0538	0,0545	0,0545	0,0538	0,0561
2	0,0608	0,0608	0,0592	0,0592	—	—
3	0,0910	0,0906	0,0906	0,0916	0,0910	—

TABLE 5.

	Sample			Total
	№ 1	№ 2	№ 3	
No. of determinations Ni	6	4	5	15
Sum of results multiplied by 10^4 (x_i = 10 000 x_i) Σx_i	3265	2400	4548	
Σx_i^2	1 777 103	1 440 252	4 136 928	
$\frac{(\Sigma x_i)^2}{Ni}$	1 776 661	144 000	4 196 861	
$\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{Ni}$	442	252	67	761

$$S' = \sqrt{\frac{761}{15-3}} \simeq 8$$

$$S = 0{,}0008\%$$

The results were treated statistically by Doerffel's method [10].

At a confidence level of 0.95 and 12 degrees of freedom, t = 2.19, i.e., in five cases in a hundred, the deviation of the percentage content found will be greater than 2.19 × 0.008% = 0.0017%.

SUMMARY

A simple method is suggested for the quantitative separation of cerium by means of sodium fluoride.

A rapid titrimetric method for the determination of cerium by means of a solution of hydroquinone is suggested. Statistical treatment of the analytical results shows the absence of any systematic error, and demonstrates the high accuracy of the results.

Determination of cerium by the suggested method takes 5-6 hr.

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DETERMINATION OF TITANIUM IN TITANIUM CARBIDE-VANADIUM ALLOYS

E. E. Kotlyar and T. N. Nazarchuk

Institute of Metalloceramics and Special Alloys, Academy of Sciences,
Ukr. SSR, Kiev

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Vanadium is known to interfere with the titrimetric and gravimetric determination of titanium. Fusion with sodium peroxide or with a mixture of sodium carbonate and potassium carbonate, with subsequent leaching of the melt with water, and also precipitation of titanium with sodium hydroxide and sodium carbonate [1,2] have been used for separating titanium and vanadium. At high vanadium contents, titanium is determined after removal of vanadium by distillation in a stream of hydrogen chloride. In the course of analyzing alloys of titanium carbide and vanadium metal, at vanadium contents greater than 30%, we checked on the fusion method with sodium peroxide subsequent leaching of the melt with water and double precipitation with sodium hydroxide. It was established in the course of this work that complete separation of titanium and vanadium cannot be achieved.

In order to separate titanium and vanadium we precipitated the latter with sodium diethyldithiocarbamate in the presence of masking agents. Both vanadium and titanium are known to form compounds with diethyldithiocrabamate which are sparingly soluble in water [3]. Chernikhov and Dobkina [4] have shown that vanadium diethyldithiocarbamate has a high stability in acid solutions. It is not formed in neutral or weakly alkaline solutions. Vanadium diethyldithiocarbamate is readily extracted by organic solvents, the best extractant in acid solutions being chloroform. Extraction of vanadium from the chloroform extract into the aqueous phase is achieved by shaking with nitric acid in the presence of hydrogen peroxide or hydrochloric acid. The method of removing vanadium from titanium by precipitating it with diethyldithiocarbamate in the presence of citric acid is recommended for the photometric determination of titanium in heat resistant alloys [5].

The aim of the work described here was a detailed study of the possibility of separating titanium and vanadium by precipitation with diethyldithiocarbamate in the presence of various masking agents. According to Pyatnitskii [6] vanadium is completely masked by tartaric acid at pH 7, and by citric acid at pH 4, 5 when a 50-fold amount of each of the acids is used. Titanium is not precipitated by diethyldithiocarbamate whatever the pH, either in the presence of tartaric or citric acids.

The problem confronting us was the direct opposite of that solved by I. V. Pyatnitskii: we had to find the pH at which vanadium would be completely precipitated by diethyldithiocarbamate in the presence of tartaric, oxalic, and citric acids and fluorides. The complex compounds of titanium with tartaric, oxalic, and citric acids, and fluorides are not decomposed by diethyldithiocarbamate, and titanium can be determined in the aqueous phase in the presence of the materials listed.

The following experiments were carried out in order to establish the pH for complete precipitation of vanadium with diethyldithiocarbamate in the presence of the masking agents. To a sulfuric acid solution of vanadium containing from 0.1-0.15 g of the latter was added masking agent in an amount 20 times that of the vanadium; the pH was adjusted to the requisite value by addition of ammonia, acetate-ammoniacal buffer of the appropriate pH value and dry sodium diethyldithiocarbamate were then added. The vanadium diethyldithiocarbamate precipitate was extracted with chloroform. The vanadium content of the aqueous phase was determined photometrically with hydrogen peroxide in the presence of sodium fluoride.

The results obtained (Table 1) show that vanadium is quantitatively precipitated with diethyldithiocarbamate in the presence of tartaric acid at pH 3-5, in the presence of citric acid at a pH not higher than 3, and in the presence of fluorides at pH 5.6. In the presence of oxalic acid vanadium remains in the aqueous phase whatever the pH, although at pH 5-6 these amounts are insignificant.

In order to check on the possibility of separating titanium and vanadium by precipitation with sodium diethyldithiocarbamate in the presence of masking agents, synthetic mixtures with the following Ti:V ratios were prepared 1:0.5, 1:1, 1:1.5. The amount of titanium was the same in all the experiments, namely 0.1 g. Appropriate amounts of masking agent were added to sulfuric acid solutions of Ti and V, the pH was adjusted to a definite value, and the vanadium diethyldithiocarbamate extracted. Titanium was determined in the aqueous phase either titrimetrically or gravimetrically.

TABLE 1. Effect of the pH of the Solution on Precipitation of Vanadium with Diethyldithocarbamate in the Presence of Masking Agents in Amounts which are 20-times that of the Vanadium

Masking agent	Tartaric acid				Citric acid				$H_2C_2O_4$				NH_4F			
pH of the solution	3	4	5	6	2.5	3	4	5	3	4	5	6	3	4	5	6
No. of extractions with chloroform	1	1-2	2-3	5-6	1-2	1-2	2-3		3-4	3-4	3	2-3	3-4	3-4	2-3	2-3
Color of the aqueous phase after extraction	colorless			traces	colorless		traces		light blue, blue	light blue	colorless		light blue		colorless	
Amount of vanadium in the aqueous solution,%	0	0	traces	5-10	0	traces	5-10		10-20	5-10	2-5	1-2			0	0

TABLE 2.

Masking agent	Amt. of titanium, g	Vanadium added, g	pH of the solution	Ti found, g	Error (absolute)	Error (relative) %
Tartaric acid	0,1104	0,0512	3—4	0,1107	+0,0004	0,3
	0,1104	0,0512	3—4	0,1110	+0,0006	0,5
	0,1104	0,1023	3—4	0,1105	0,0001	0,1
	0,1104	0,1023	3—4	0,1107	0,0001	0,2
	0,1104	0,1533	3—4	0,1101	—0,0003	0,3
	0,1104	0,1573	3—4	0,1105	+0,0001	0,1
	0,1125	0,0512	5	0,1188	0,0065	5,5
	0,1125	0,0512	5	0,1160	0,0035	3
	0,1125	0,1023	5	0,1183	0,0065	5.5
	0,1125	0,1533	5	0,1170	0,0045	4,0
	0,1125	0,1533	5	0,1165	0,0040	3,5
Citric acid	0,1104	0,1023	3—4	0,1145		3,5
	0,1104	0,1023	3—4	0,1168		6,0
	0,1104	0,1533	3—4	0,1150		4,0
	0,1104	0,1533	3—4	0,1145		3,5
Oxalic acid	0,1104	0,0512	5—6	0,1111		0,6
	0,1104	0,1023	5—6	0,1143		3,0
	0,1104	0,1023	5—6	0,1132		2,5
	0,1104	0,1023	5—6	0,1135		3,0

As the results obtained show (Table 2), optimum separation of titanium and vanadium with diethyldithiocarbamate is achieved in the presence of tartaric acid at pH 3-4, and in the presence of ammonium fluoride at pH 5-6. Satisfactory results are obtained in the presence of citric acid at pH 2.5-3. The amount of vanadium in the aqueous phase increases with increasing pH.

Method for Determining Titanium in TiC-V Alloys. A 0.1-0.2 g of alloy is dissolved in a mixture of 20 ml H_2SO_4 (1:4) and 5 ml HNO_3 (sp.gr. 1.43). When dissolution is complete the solution is evaporated to the appearance of thick SO_3 fumes. 25 ml of 1 M tartaric acid solution is added to the cooled solution. By adding ammonia solution dropwise the pH of the solution is adjusted to 3-4; 20 ml of acetate-ammoniacal buffer with pH 3-4 is added. The solution is transferred to a separating funnel and dry sodium diethyldithiocarbamate added in small portions. The yellow-orange colored precipitate of vanadium diethyldithiocarbamate is extracted with chloroform. The pH of the aqueous layer is checked by universal indicator paper, and, if necessary, 1-2 drops of hydrochloric acid added; precipitation of vanadium with diethyldithiocarbamate is then repeated. After the second precipitation the aqueous layer which is free from vanadium is transferred to a beaker, and boiled until the solution clears; 20 ml of H_2SO_4 (1:1) is added and titanium determined by one of the known methods. 1-2 g of ammonium fluoride can be used instead of tartaric acid; when ammonium fluoride is used the pH should be 5-6. The titanium in the aqueous phase is determined titrimetrically.

TABLE 3.

Sample	C_{total}, %	V, %	Ti found, %			
1*	18,00	4,45	74,40:	75,09	74,85	
2*	18,60	8,20	71,43;	71,35		
3*	16,40	16.50	63,43;	63,04;	63,24;	63,40
4*	15,20	23,0	57,65;	57,57;	57,45	
5*	18,50	42,0	39,50;	39,20		
6*	14,7	30,0	51,90;		51,45	
7*	8,3	57,40	35,02;		34,74	
8*	5,7	64,60	28,94;		29,10	
9*	4,7	74,70	19,16;		19,00	
10*	2,4	88,5	10,0;		10,14	

Vanadium can be determined titrimetrically on a separate aliquot without removal of the titanium, or in the chloroform extract.

Results of analysis of alloys of titanium carbide and vanadium are given in Table 3.

SUMMARY

Conditions for precipitating vanadium with sodium diethyldithiocarbamate in the presence of tartaric, citric, and oxalic acids, and ammonium fluoride have been studied. Complete separation of titanium and vanadium by precipitation with sodium diethyldithiocarbamate is possible in the presence of citric, or tartaric acid or ammonium fluoride at a pH of 2-3, 3-4, and 5-6 respectively.

A method has been developed for the analysis of alloys of titanium carbide and vanadium metal.

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CONDITIONS FOR SEPARATION OF ARSENTIC AND PREPARATION OF THE BLUE ARSENOMOLYBDATE COMPLEX

G. A. Butenko, V. P. Korzh, and E. M. Rodionova

Institute of Ferrous Metallurgy, Academy of Sciences, Ukr. SSR, Dnepropetrovsk

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Having studied conditions for arsenic determination, Finkel'shtein and Kryuchkova [1] concluded that its determination by distillation of arsenic chloride from a hydrochloric acid solution and absorption with water leads to an appreciable loss of arsenic (from 12 to 40%); these authors recommend therefore that the arsenic chloride be absorbed with a 1% hydrogen peroxide solution. Published information [2-5] indicates that the method outlined for separation of small amounts of arsenic with absorption in water is the best method. We have not observed any loss of arsenic on using this method over a period of several years.

In order to make a comparative study of the absorption of arsenic chloride by water and 1% hydrogen peroxide we carried out a series of experiments on standard samples of agglomerates, cast iron, and steel.

Removal of excess oxidizing agent from the distillate by evaporation to dryness lengthens the determination. Moreover, as published data show, prolonged heating and non-observance of temperature conditions during evaporation to dryness can lead to partial volatilization of arsenic. In this connection, for comparison, we removed excess hydrogen peroxide by evaporation to dryness with nitric acid, and by addition of permanganate solution.

As the results in Table 1 show, positive results were obtained both when arsenic chloride was absorbed with water and with 1% hydrogen peroxide solution. We did not detect any loss in arsenic during its distillation into water, just as we detected no loss previously during numerous experiments.

Finkel'shtein and Kryuchkova explain the loss of arsenic during distillation in water by the fact that the equilibrium $AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$ is shifted to the left as the concentration of the hydrochloric acid which distills over when arsenic chloride increases, while the latter, as a result of these conditions, partially evaporates from the aqueous solution. In the presence of hydrogen peroxide, arsenic acid is formed, and this leads to a shift of the equilibrium to the right.

In order to shift the equilibrium to the right and thereby avoid the possibility of loss of arsenic, we used a solution of ammonia and a solution of sodium hydroxide instead of 1% hydrogen peroxide for absorbing arsenic chloride, the amounts of the respective alkalis taken being sufficient to ensure an alkaline reaction until the end of the distillation of the arsenic.

The results given in Table 1 show that the amounts of arsenic obtained in these cases are again of the same order as when the arsenic chloride is absorbed with water and hydrogen peroxide.

On the basis of Raoult's law and psychrometry we calculated the theoretical possibility of loss of arsenic during its distillation from a hydrochloric acid solution and its absorption with water.

Assuming that all the arsenic is present in the distillate as arsenic chloride and that a small current of carbon dioxide is passed through the solution during distillation, the calculated loss of arsenic amounts to about 0.3%, i.e., it does not, in practice, have any effect on the quantitative determination of arsenic.

Finkel'shtein and Kryuchkova [1] indicate that in the presence of sodium chloride, the stability and reproducibility of the optical density of the solutions deteriorate, while at an appreciable ammonium chloride concentration, the optical density decreases significantly. Since we neutralized the hydrochloric acid distillate with ammonia in the technique we use, it was necessary to check the effect of the salts indicated on the optical density. For this purpose varying amounts of sodium, ammonium, and potassium chlorides, and sodium and potassium sulfates were added to the solution being photometrically measured.

TABLE 1. Absorption of Arsenic Chloride

Arsenic taken for distillation, mg	Arsenic found				
	water	1% H_2O_2 solution		ammonia solution	sodium hydroxide solution
		excess H_2O_2 removed with permanganate	excess H_2O_2 removed by evaporation with HNO_3 to dryness		
0.8	0.79; 0.79	0.81; 0.79	0.81; 0.80	0.80; 0.79	0.81; 0.81
	0.80; 0.81	0.80; 0.81	0.79; 0.80	0.80; 0.80	0.80; 0.82
0.4	0.40; 0.39	0.38; 0.40	0.40; 0.39	0.41; 0.40	0.40; 0.41
	0.39; 0.40	0.41	0.41	0.40	
0.2	0.21; 0.20	0.20; 0.20	0.19; 0.20	0.20; 0.21	0.19; 0.21
	0.20; 0.21	0.19; 0.21	0.19	0.20	
Agglomerate, standard					
sample No. 211	0.128; 0.126	0.13; 0.128	0.127; 0.13		
0.125% As	0.127; 0.126	0.126	0.129	—	—
Agglomerate, standard					
sample KBK	0.116; 0.118	0.117; 0.12	0.115; 0.117		
0.113% As	0.117	0.116	0.12	—	—
Cast iron, standard					
sample No. 64	0.149; 0.152	0.15; 0.152	0.152; 0.154	—	—
0.152% As	0.15				
Steel, standard					
sample No. 199					
0.117% As	0.115; 0.118	0.116; 0.118	0.119; 0.115	—	—

TABLE 2. Effect of NaCl, NH_4Cl, KCl, and Na_2SO_4 on the Optical Density of Solutions of the Blue Arsenomolybdate Complex

Arsenic taken, mg	Amt. of salt added, g	Arsenic found (mg) in the presence of the salts:				
		NaCl	NH_4Cl	KCl	Na_2SO_4	K_2SO_4
0,05	0,5	0,05; 0,051	0,051; 0,05 0,5			
0,1		0,101; 0,101	0,104; 0,1	0,1; 0,101	—	—
0,05	1,0	0,051; 0,05 0,5	0,05; 0,05			
0,1		0,1; 0,108 0,104; 0,106	0,1; 0,102	0,1; 0,1	0,102; 0,101	0,102; 0,102
0,05	2,0	0,056; 0,068	0,05; 0,051 0,05			
0,1		0,106; 0,106	0,1; 0,101	0,101; 0,1	0,103; 0,101	—
0,05	3,0	0,061; 0,06	0,05; 0,052 0,05			
0,1		0,132; 0,112 0,142	0,101; 0,1	0,1; 0,102	0,102; 0,102	0,101; 0,102
0,05	4,0	0,05; 0,051	0,051; 0,05			
0,1		0,1; 0,098	0,102; 0,101	0,097; 0,098	0,101; 0,102	—
0,05	5,0	0,042; 0,044	0,049; 0,05			
0,1		0,069; 0,067	0,098; 0,097	0,08; 0,081	0,102; 0,102	0,102; 0,102
0,1	7,0	0,022; 0,023	0,096; 0,1	0,036; 0,038	0,101; 0,103	0 101; 0,102
0,1	10,0	Noblue color	0,108; 0,11	No blue color	0,102; 0,104	—

The results given in Table 2 show that the reproducibility of the optical density deteriorates in the presence of sodium and potassium chlorides. Starting at a value of 5 g and going upward, the optical density decreases significantly, while in the presence of 10 g of the salts indicated the blue arsenomolybdate complex is not formed at all. Ammonium chloride and sodium sulfate in amounts up to 10 g, and potassium sulfate in amounts up to 7 g, do not affect the optical density.

The different effect shown by the chlorides and sulfates of the alkali metals is explained by the fact that arsenic chloride is capable of forming the compounds $M(AsCl_4)$, $M_2(AsCl_6)$ [6] with the chlorides of the univalent metals.

Finkel'shtein and Kryuchkova recommend that the distillation be carried out without passage of carbon dioxide or nitrogen. Our many years experience has shown that it is much more convenient to pass carbon dioxide through the solution at a rate of 1-2 bubbles per second during distillation. Passage of carbon dioxide promotes volatilization of the arsenic, prevents suck back of the distillate in the condenser, and helps to maintain smooth and uniform boiling. This is particularly convenient when several distillation setups are in simultaneous use.

Finkel'shtein and Kryuchkova indicate that the acidity of the solution being photometrically measured should lie within the limits 0.1-0.5 N. One of the authors of the present article [7] during a study of the effect of acidity and the amount of ammonium molybdate on the color intensity of blue arsenomolybdic acid, established that the amount of ammonium molybdate has an essential influence on the maximum permissible acidity of the solution, the permissible acidity being higher the greater the excess of ammonium molybdate used. Using the amount of molybdate recommended by Finkel'shtein and Kryuchkova in their analytical procedure for arsenic determination, the permissible acidity should lie within the range 0.2-0.35 N; at 0.1 N reduction of excess molybdate will occur, while at 0.4 N and upward, appreciable weakening of the color will be observed.

SUMMARY

The method of distilling arsenic chloride from a hydrochloric acid solution with subsequent absorption in water gives completely reliable results for low arsenic contents.

When arsenic chloride is absorbed with hydrogen peroxide solution, excess of the latter can be removed with permanganate solution, without resorting to evaporation to dryness.

Alkali metal chlorides lead to a deterioration in the stability and reproducibility of the optical density of the solution, while at relatively high contents of these salts the optical density decreases significantly. Ammonium chloride and alkali metal sulfates do not affect the optical density.

Passage of carbon dioxide through the solution during distillation improves the conditions for volatilization of arsenic chloride.

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2,3-DIMERCAPTOPROPIONIC ACID AS A REAGENT FOR MOLYBDENUM

A. I. Busev, Chang Fan, and Z. P. Kuzyaeva

M. V. Lomonosov Moscow State University

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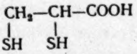
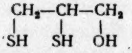
2,3-Dimercaptopropionic acid  $\underset{SH}{CH_2}-\underset{SH}{CH}-COOH$ and dimercaptopropanol (BAL)  $\underset{SH}{CH_2}-\underset{SH}{CH}-\underset{OH}{CH_2}$ contain a combination of atoms which ensure that they interact with sexi- and quinquevalent molybdenum to form yellow colored compounds [1]. Both compounds permit detection of very small amounts of molybdenum; nevertheless, dimercaptopropanol is less suitable than 2,3-dimercaptopropionic acid for the photometric determination of molybdenum, as our experiments have shown. Accordingly, we only studied 2,3-dimercaptopropionic acid in detail as a reagent for molybdenum.

Dibromopropionic acid was used as starting material for preparation of 2,3-dimercaptopropionic acid [2]. The yield was about 30%.

Experiments showed that sodium molybdate reacts with excess 2,3-dimercaptopropionic acid at acidities ranging from pH 6 to 6 N HCl. A greenish-yellow color appears immediately in weakly acid (pH 3) and strongly acid (0.2 N HCl) media. Under such conditions quinquevalent molybdenum gives a yellow colored compound with the reagent.

The quinquevalent molybdenum compound has a less intense color than that of sexivalent molybdenum (under comparable conditions).

In the presence of a relatively small excess of reagent (e.g., a ten-fold excess in moles) the optical density of solutions of the sexi- and quinquevalent molybdenum compounds formed (about 10^{-4} M Mo^{VI} or Mo^{V}) attains a constant value very slowly at pH 1.3-4 (e.g., after 1 hr 30 min). When the reagent is present in an appreciable excess (e.g., 100-fold and more in moles) the optical density acquires a constant value in 10 min over the acidity range pH 2 to 5 N HCl, and does not change over a period of more than three hours.

After reaching a constant value, the maximum optical density is observed at pH 3.5-5.0 in the case of the sexivalent molybdenum compound, while in the case of the quinquevalent molybdenum compound the maximum optical density is observed at pH 1.4-4.7 (for a ten-fold molar excess of reagent).

Absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid are shown in Fig. 1. All these curves were obtained using a ten-fold molar excess of reagent. The optical density was measured when it had reached a constant value. The absorption curve of the solution of the sexivalent molybdenum compound has a maximum at 360 mμ after 20 min at pH 4.84 (Fig. 1, curve 1). After 24 hr the same solution has an absorption maximum at 330 mμ (Fig. 1, curve 2). It coincides with the absorption maximum of solutions of the quinquevalent molybdenum compound at pH 1.4 (Fig. 1, curve 4).

The maximum of the absorption curves of solutions of the sexivalent molybdenum compound after 21 hr at pH 1.05 (Curve 3, Fig. 1) and of solutions of the quinquevalent molybdenum compound 10 min after preparation at pH 1.4 (Fig. 1, curve 4) also coincide.

Solutions of 2,3-dimercaptopropionic acid hardly absorb any light at 360 mμ and 330 mμ.

The absorption maximum and the apparent molar extinction coefficient of solutions of the compounds formed on mixing solutions of quinquevalent and sexivalent molybdenum with 2,3-dimercaptopropionic acid at pH 1 and in a 3 N HCl medium almost coincide with each other (Table 1). This gives grounds for assuming that at pH 1 and in a 3 N HCl medium, excess of reagent reduces sexivalent molybdenum to the quinquevalent state, forming a colored compound with it. The reduction rate is strongly dependent on the acidity of the solution.

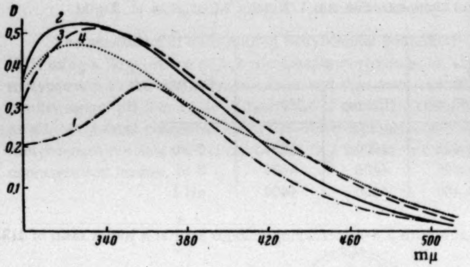


Fig. 1. Absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid. The concentration of Mo^{VI} and Mo^{V} was the same in all the solutions and equal to 1.03×10^{-4} M; the reagent concentration was 10^{-3}M. 1) Mo^{VI}, pH 4.84, 10 min after preparation of the solution; 2) Mo^{VI}, pH 4.84, 28 hr after preparation of the solution; 3) Mo^{VI}, pH 1.05, 21 hr after preparation of the solution; 4) Mo^{V}, pH 1.4, 10 min after preparation of the solution.

The molar ratios which obtain during the interaction of sexivalent and quinquevalent molybdenum with 2,3-dimercaptopropionic acid were established by the isomolar series method. Different volumes of a 0.01069 M solution of sodium molybdate or of a quinquevalent molybdenum salt (the latter in 1 N HCl) were mixed with a neutral 0.01089 M solution of 2,3-dimercaptopropionic acid so that the sum of the molar concentrations of both components in the final volume was constant and equal to 8.71×10^{-4}M.

The 2,3-dimercaptopropionic acid concentration in the original solution was determined by potentiometric titration with 0.01 N NaOH.

Experiments were carried out at pH 0.92 and 4.84 (Figs. 2, 3) in the case of sexivalent molybdenum. Buffer solutions with pH 0.92 and 3.84 were used for adjusting the pH to the required value.

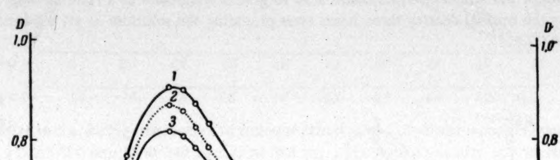


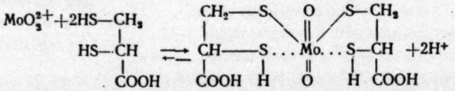
Fig. 2. Molar ratio during interaction of sexivalent molybdenum with 2,3-dimercaptopropionic acid (pH 0.92). 1) At 329 mμ; 2) at 350 mμ; 3) at 358 mμ. The optical density was measured 20 min, 3 hr, and 24 hr after preparation of the solutions.

The optical density was measured at 329, 350, and 358 mμ, 10 min, 3 hr, and 24 hr after preparation of the solutions. Experiments with quinquevalent molybdenum were carried out at pH 0.92 (Fig.4).

TABLE 1. The Final Molybdenum Concentration was 1.03×10^{-4}M

Valence of molybdenum	D (l = 1 cm)		ε		Acidity
	329 mμ	360 mμ	329 mμ	360 mμ	
Mo^{V}	0.430	0.435	4200	4200	3 M
	0.450	0.460	4400	4400	3 M
Mo^{VI}	0.460	0.460	4400	4400	pH 1

At pH 0.92 sexivalent molybdenum initially reacts with 2,3-dimercaptopropionic acid at a molar ratio of 1:2, probably according to the following equation:



After 24 hr the molar ratios altered (at pH 4.84) and proved to be 2:5. This result can be explained by assuming that sexivalent molybdenum is reduced to the quinquevalent state (one mole of 2,3-dimercaptopropionic acid is expended on two moles of sexivalent molybdenum), and that subsequently two moles of quinquevalent molybdenum react with four moles of 2,3-dimercaptopropionic acid to give a compound at a ratio of 1:2. The molar ratios determined by measuring the optical density three hours after preparing the solutions at pH 4.84 proved to be intermediate between 1:2 and 2:5 (Fig. 3).

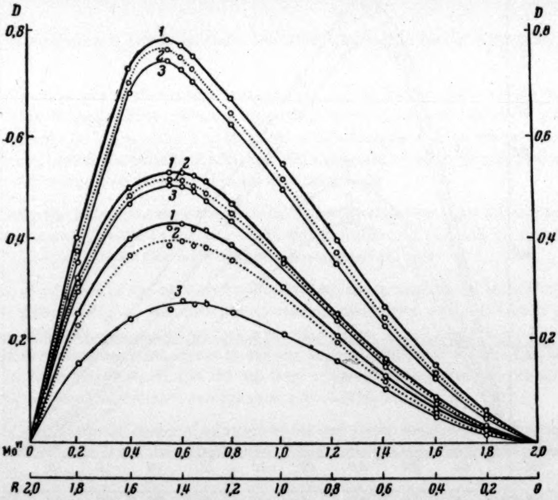


Fig. 3. Molar ratios during interaction or sexivalent molybdenum with 2,3-dimercaptopropionic acid (pH 4.84). 1) At 329 mμ; 2) at 350 mμ; 3) at 358 mμ. The optical density was measured 10 min, 3 hr, and 24 hr after the solutions had been prepared.

The maximum optical density in experiments with quinquevalent molybdenum was found at a molar ratio of molybdenum to 2,3-dimercaptopropionic acid of 1:2 (Fig. 4). The reaction, presumably, proceeds according to the equation:

$$Mo_2O_3^{4+} + 4CH_2(SH) - CH(SH) - COOH \rightleftharpoons Mo_2O_3[S - CH_2 - CH(SH) - COOH]_4 + 4H^+$$

The possibility of determining molybdenum photometrically was studied in a medium of 3 N HCl and 0.2 N HCl, using a large excess of 2,3-dimercaptopropionic acid, which, at such an acidity completely and rapidly reduces molybdenum to the quinquevalent state and then forms a sufficiently intensely yellow colored compound. Over the acidity ranges pH 2 to 1.0 N HCl, and 1.5 N to 5 N HCl, the optical density of the solutions obtained hardly changes at all. At a final concentration of 2,3-dimercaptopropionic acid of 10^{-2}M, the optical density of 10^{-4}M solutions of molybdenum reaches a maximum value in 3 hr, and this value remains almost constant on increasing the reagent concentration further.

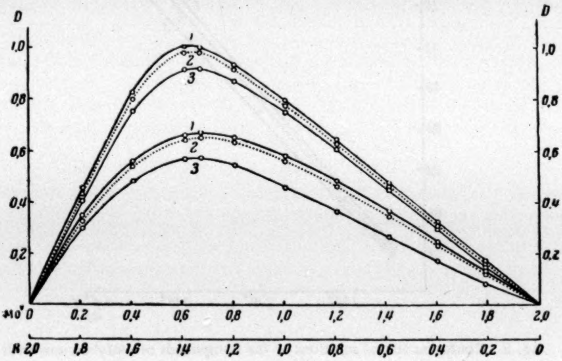


Fig. 4. Molar ratios during interaction of quinquevalent with 2,3-dimercaptopropionic acid (pH 0.96). 1) At 329 mμ; 2) at 340 mμ; 3) at 358 mμ. The optical density was measured 10 min, and 24 hr after the solutions had been prepared.

A calibration curve was constructed as follows: 5 to 0.5 ml aliquots of 2.5×10^{-3}M sodium molybdate solution were introduced into 25 ml flasks, and 6.5 ml of concentrated hydrochloric acid and 3.75 ml of 0.1 M 2,3-dimercaptopropionic acid (150-fold excess with respect to molybdenum) added to each, the volumes of the solutions were made up to the mark with water and the flasks shaken. The hydrochloric acid concentration of the final solution was about 3 N.

The optical density was measured after 10 min with respect to water in a cell with a path length of 1 cm, using a SF-4 spectrophotometer at 329 mμ or at 350 mμ. The solutions conform well to Beer's law over the range 2.5 μg Mo/ml to 39.4 μg Mo/ml.

Molybdenum was determined photometrically under the same conditions as those used for constructing the calibration curve.

Copper ions give a dark-blue precipitate with the reagent and interfere with molybdenum determination. Thiourea cannot be used for masking copper since nonreproducible and incorrect results are obtained. Divalent iron does not interfere with molybdenum determination; trivalent iron gives a dark-blue color which disappears on adding excess reagent. Divalent mercury forms a white, clotted precipitate with the reagent.

Lead, chromium, aluminum, nickel, cobalt, zirconium, titanium, tungsten, zinc, manganese, and barium ions do not give a color or precipitate with the reagent. Nevertheless, molybdenum cannot be determined in the presence of these elements, since a white turbidity appears, the amount of which increases with time.

We also studied the possibility of determining molybdenum in the presence of foreign elements in a medium of 0.2 N HCl. The calibration curve was constructed as in the previous case. These solutions also conformed well to Beer's law over the range 4 μg/ml to 40 μg/ml. Water was used as the reference solution (Fig. 5).

Satisfactory results were obtained in the presence of large amounts of zirconium, titanium, chromium, cobalt, nickel, aluminum, zinc, and manganese (Table 2). In the presence of chromium the optical density should be measured immediately, since after two hours high results are obtained. Tungsten is precipitated as tungstic acid; after filtering off the latter low results are obtained for molybdenum. Lead is precipitated as its chloride. When bismuth is present a turbidity appears. Divalent copper and univalent mercury interfere. Trivalent iron should be reduced to the divalent state with ascorbic acid.

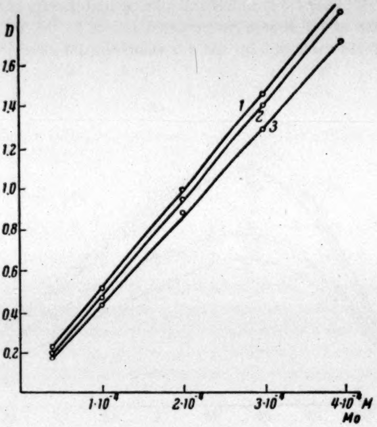


Fig. 5. Conformation of solutions of the compounds of molybdenum with 2,3-dimercaptopropionic acid in 0.2 N HCl to Beer's law; Mo:R = 1:150. 1) 330 mμ; 2) 360 mμ; 3) 380 mμ.

TABLE 2. (0.24 mg Mo taken; final acid concentration 0.2 N HCl)

Foreign elements, mg	Mo found, mg	Error, mg	Foreign elements, mg	Mo found, mg	Error, mg
10 Zn	0,24	0,00	10W**	0,21	−0,03
5 Ti	0,24	0,00	20Zn	0,24	0,00
20 Cr°°	0,24	0,00	20Mn	0,24	0,00
2 Bi	0,47	+0,23	40Fe^{+3}***	0,26	+0,02
40 Ni	0,24	0,00	40Fe^{+3}****	0,26	+0,02
20 Co	0,23	−0,01	40Fe^{+3}°	0,47	+0,23
20Pb*	0,19	−0,05	20Al	0,23	−0,01

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* After filtering off the $PbCl_2$ precipitate.

** After filtering off the turbidity from tungstic acid.

*** In the presence of 0.77 g ascorbic acid.

**** In the presence of 1.13 g ascorbic acid.

° In the presence of 0.25 ml of concentrated H_3PO_4.

°° Results were high by 0.02 mg after 2 hr.

SUMMARY

The interaction of 2,3-dimercaptopropionic acid with sexi- and quinquevalent molybdenum has been studied. It has been shown that molybdenum can be determined photometrically in the presence of a number of elements.

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A STUDY OF THE INTERACTION OF MOLYBDENUM WITH 8-MERCAPTOQUINOLINE

N. A. Agrinskaya and V. I. Petrashen'

Novocherkask Polytechnical Institute

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A number of papers devoted to the analytical application of 8-mercaptoquinoline have been published recently [1-4]. The composition, as determined by chemical analysis, of the compounds formed between 8-mercapotquinoline and various cations [4,5] cannot completely characterize the processes which occur in solution. The work described here is devoted to a study of the interaction of sexivalent molybdenum and 8-mercaptoquinoline (thiooxine) in solution, and to the determination of the composition and stability of the compound formed.

EXPERIMENTAL

Measurements were carried out on a FEK-M colorimeter and on a PPTV-1 potentiometer. Solutions were prepared by dissolving the recrystallized salts in twice distilled water.

Potentiometric Method. Thiooxine hydrochloride possesses reducing properties. In order to establish the amount of thiooxine which is sufficient for reducing sexivalent molybdenum, the change in the emf of the system Mo^{VI}/Mo^{x} during titration of a hydrochloric acid solution of molybdate (3 N) was established. A concentration circuit was set up in which a platinum electrode in a molybdate solution (Mo^{VI}) served as anode, while the cathode was a platinum electrode in a molybdate (Mo^{VI}) solution which was being titrated with an equimolar thiooxine solution. Completion of reduction was determined on the basis of a sharp change in potential.

As Fig. 1 shows the maximum emf change was observed on adding one mole of thioxine to one mole of molybdate. Thus sexivalent molybdenum is reduced by thiooxine to lower oxidation states.

We used an optical method for determining the stoichiometric coefficients of the reaction between molybdate and thiooxine in toluene.

Optical Method. When neither the composition of the compound formed or its state in solution are known, it is possible, using the method of limiting logarithms, to establish the number of coordinated groups in the compound.

We represent the reaction which we are interested in as follows:

$$n\,MoO_xZ^y + m\,[C_9H_6NS]^- \rightleftarrows (MoO_xZ^y)_n\ (C_9H_6NS)_m \qquad (1)$$

where MoO_xZ_y is the ion containing the reduced molybdenum. The equilibrium constant of this reaction is equal to:

$$K = \frac{[A]^n\,[B]^m}{[A_nB_m]}\,, \qquad (2)$$

where A is $[A]-[MoO_xZ^y]$, and [B] is $[B]-[C_9H_6NS]$. In logarithmic form: $\log K = n \log [A] + m \log [A_nB_m]$.

or

$$\lg [A_nB_m] = n \lg [A] + m \lg [B] - \lg K. \qquad (3)$$

When the concentration of one of the components, e.g., [A], is constant while the concentration of [B] alters, then $\log [A_nB_m]$ will be a linear function of $\log [B]$.

If the optical density D is used as a characteristic of the change in concentration $[A_nB_m]$, then log D should be a linear function of $\log [B]$.

On constructing the curve log D−log [B] we obtain a straight line, the tangent of the slope of which gives the value of n. m can be determined in exactly the same way.

The concentration of one of the components of the reaction was kept constant while that of the other component was varied, and the optimum ratio of the reactants determined.

A series of experiments was carried out with solutions of sexivalent molybdenum. The procedure adopted was as follows: concentrated hydrochloric acid was added to a molybdate (VI) solution (until the normality of the final solution was 2.56-3.50); this was followed by thiooxine solution and toluene. The mixture was shaken for 5 min. The organic layer was then removed and its optical density measured at 420 mμ.

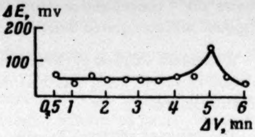

Fig. 1. Potentiometric titration of 5.0 ml of 0.00058 M molybdenum solution with 0.00058 M thiooxine solution.

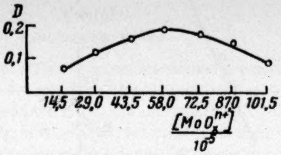

Fig. 2. Change in optical density with change in thiooxine concentration when the molybdenum (VI) concentration is kept constant.

The change in optical density with changes in molybdenum (VI) concentration (while the thiooxine concentration is constant) was found to have a maximum value at a ratio of 1:1, as Fig. 2 shows. In the experiments where this ratio was high, the optical density fell.

This fact shows that the colored compound is formed, apparently, between the reduced molybdenum and the residue of unoxidized thiooxine.

We assumed that reduction of sexivalent molybdenum by thiooxine proceeded to the quinquevalent state. This assumption is supported by the fact that Mo^V obtained by reduction with mercury metal in hydrochloric acid solution (3N) [10], gave an exactly similar colored compound with thiooxine as Mo^{VI}. The maximum absorption of this compound was also found to occur at 420 mμ.

In addition, a study of the optical density at a constant thiooxine concentration and varying Mo^V concentrations showed (Fig. 3) that the optical density remains constant after the maximum value has been reached. Changes in optical density with changes in molybdenum concentration for a constant thiooxine concentration are given in Table 1.

TABLE 1. Relation between Optical Density and Molybdenum Concentration (At a constant thiooxine concentration of 0.0378 g.ion liter)

Mo^V concentration, M	$-\log[MoO_xZ_y]$	D	-log D	n	Mo^V concentration, M	$-\log[MoO_xZ_y]$	D	-log D	m
$58 \cdot 10^{-7}$	5.24	0.025	1.61		$69.6 \cdot 10^{-6}$	4.17	0.120	0.92	
$11.6 \cdot 10^{-6}$	4.93	0.057	1.25		$92.8 \cdot 10^{-6}$	4.03	0.145	0.75	
$23.2 \cdot 10^{-6}$	4.64	0.085	1.07		$11.6 \cdot 10^{-5}$	3.93	0.120	0.92	
$46.4 \cdot 10^{-6}$	4.39	0.100	1.00	1.93					

The changes in optical density with changes in thiooxine concentration while the Mo^V concentration is constant are given in Table 2.

As Tables 1 and 2, and Figs. 3 and 4, show, the coefficients n and m in equation 1 are equal to 2.

Radiometric Method. We decided it would be expedient to calculate $K_{instab.}$ of the compound obtained in toluene by a radiometric method, by establishing the partition coefficient of molybdenum thiooxinate between the organic and aqueous phases.

Molybdenum thiooxinate was prepared under the optimum reaction conditions [4,5]. Having determined the concentration of molybdenum in the aqueous phase, we established the equilibrium concentration of molybdenum not entering into a compound with thiooxine. Having determined the molybdenum concentration of the organic phase, we established the concentration of the compound of molybdenum with thiooxine.

The experimental procedure was as follows. Water was added to solutions containing different amounts of Mo^{99} so that the total volume in each case was 5 ml, 1.5 ml of concentrated HC-; 0.38 ml of thiooxine (5% solution), and 1.5 ml of toluene were then added and the mixtures shaken for 3 min. The organic and aqueous phases were removed from each other and evaporated separately; the activity of the dry residues was then measured on a counter of the VSP-1957-2753 type.

The molybdenum concentration can be estimated from the calibration curve constructed within the coordinates Mo^{99} concentration–activity (cpm). The background was calculated before each determination.

A standard solution of $(NH_4)_2MoO_4$ prepared from an aliquot of active MoO_3 was used for constructing the calibration curve.

The value of arbitrary $K_{instab.}$ calculated by means of equation 2 (using mean values) was 7.80×10^{-4}.

The partition of molybdenum was studied in solutions whose acidity with respect to HCl was 1.15, 2.18, and 3.25 N. Under these conditions the stability of the compound proved to be the same.

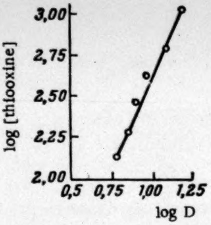

Fig. 3. Relation between log optical density and log thiooxine concentration.

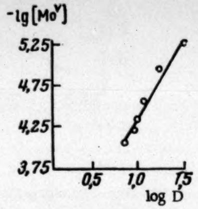

Fig. 4. Relation between log optical density and log Mo^V concentration.

TABLE 2. Relation between Optical Density and Thiooxine Concentration (At a Mo^V concentration of 0.000058 g.ion liter)

Thiooxine concentration, M	-log [thiooxine]	D	-log D	m	Thiooxine concentration μg/ml	-log [thiooxine]	D	-log D	m
$8.56 \cdot 10^{-4}$	3.07	0.075	1.15		$34.24 \cdot 10^{-4}$	2.46	0.135	0.87	
$17.12 \cdot 10^{-4}$	2.76	0.080	1.10		$51.36 \cdot 10^{-4}$	2.28	0.138	0.86	
$25.68 \cdot 10^{-4}$	2.69	0.125	0.90	2	$68.48 \cdot 10^{-4}$	2.16	0.140	0.76	

TABLE 3. Determination of $K_{instab.}$ by a Radiometric Method

Molybdenum concentration, μg/ml	No. of impulses, cpm		Equilibrium concentration of molybdenum, g. ion/liter	Excess thiooxine concentration, g. ion/liter	Concentration of the complex g. ion/liter
	aqueous phase	organic phase			
1.5	100				
3.0	203				
6.0	426				
3.0	18	180	0.155	0.0140	2.70
3.0	12	170	0.230	0.0137	2.40
3.6	34	230	0.400	0.0105	3.30
3.6	40	240	0.150	0.0145	3.60
3.0	5	105	0.080	0.0153	2.85
3.0	7	180	0.100	0.0155	2.55

Composition of the Compound Formed between Molybdenum and Thiooxine. Having established the stoichiometric coefficients of the compound of molybdenum with thiooxine, and the stability of the compound formed, we decided to attempt to establish the formula of this compound. For this purpose it was necessary to establish the valence of molybdenum in the compound.

Published information on the valence of molybdenum in this compound is contradictory.

Bankovskii in one of his earlier papers [5] gives the following formulas for compounds of molybdenum with thiooxine in a weakly acid medium (pH 2÷3):$Mo_2O_3(C_9H_6NS)_2 \cdot H_2O$–a compound with a green color.

In the presence of strong reducing agents ($TiCl_3$, $SnCl_2$) the yellow colored compound $MoO(C_9H_6NS) \cdot {}^1/_2H_2O$– is formed.

The valence of molybdenum in the first compound is, presumably, four while in the second it is three. In more recent papers Bankovskii gives the following formula for the compound of molybdenum with thiooxine:$MoO_2(C_9H_6NS)_2 \cdot H_2O$. The valence of molybdenum in this compound is obviously six. Such a compound is formed at pH 2-3 and lower [4].

Bankovskii established the composition of the thiooxinates by a preparative method.

We [6], like Bankovskii, have pointed out that thiooxinates of different colors are formed depending on the acidity. In weakly acid media orange-green colored thiooxinates are formed, while in more acid media yellow to brown-reddish thiooxinates are formed. Nevertheless we are not inclined to explain the difference in color of the thiooxinates formed by differences in the degree to which molybdenum is reduced, but consider it more likely that it is determined by differences in the state of the molybdenum as a function of the degree of acidity.

According to published information, and according to our studies [7, 8], molybdenum forms complex compounds which are anionic in character when the acid concentration exceeds 1.0 N (with respect to HCl), while over the acidity range 0.1-1 N molybdenum is found in the form of MoO_2^{2+}.

Chloride complexes of quinquevalent molybdenum are described in a paper by Babko and Get'man [9]. The authors also point out changes in color of solutions containing molybdenum with changes in HCl concentration, and, on the basis of the character of the spectrophotometric curves, state that Cl^- does not simply enter into the inner coordination sphere of the complex, but expels oxygen ions. Babko and Get'man also put forward the suggestion that quinquevalent molybdenum exists in the form MoO_2^+ up to a HCl concentration of 2 N. On increasing the HCl concentration above 3 N, MoO^{3+} will dominate. The MoO^{3+} is capable of reacting with Cl^- even in dilute solutions with formation of unstable and colorless complexes of $MoOCl_2^+$ and $MoOCl^{2+}$, while in the presence of a large excess of Cl^- the colored complex $MoOCl_3$ is formed.

These results are in good agreement with the ones we obtained by a kinetic method for Mo^{VI} [7]. Total $K_{instab.} = 5 \times 10^{-3}$ for $MoOCl_3$ [9].

K for the first dissociation stage, obviously, has a large value. It is possible that the reaction with thiooxine proceeds as follows in the aqueous phase:

$$n\, MoOCl_3 + m\, K(C_9H_6NS) = \underbrace{[MoOCl_2]_n\, [C_9H_6NS]_m}_{\swarrow} + KCl.$$

The very low solubility of molybdenum thiooxinate (precipitates are formed even in 4.0 N HCl) [6,4] supports this assumption.

It is probable that the differences in the color of molybdenum thiooxinates is determined by differences in the composition of the chloride complex ions which interact with thiooxine.

During a check on the effect of reducing agents on the nature of the interaction of molybdenum with thiooxine, it was found that ascorbic acid present in a sample does not alter the optical density of the compound formed with thiooxine as compared with the optical density of the compound obtained in the absence of any foreign reducing agents. It is obvious that thiooxine itself reduced Mo^{VI} to Mo^{V}. We assumed the following mechanism for the reaction: Mo^{VI} is reduced by thiooxine in a hydrochloric acid medium to Mo^{V}, and the latter in the form of a chloride complex cation reacts with excess thiooxine.

The results obtained by the preparative method published by Bankovskii support this assumption. In a strongly acid medium (HCl 1:1) he obtained a compound containing 16.4% Mo, 18.14% Cl, and 4.95% N; in a weakly acid medium (pH 2-3 and in more acid regions) the compound obtained 20.64% Mo, 6.29% N, and 13.67% S.

Thus on the basis of what has been said above it can be assumed that the compound of molybdenum with thiooxine in a medium of 2.5-3.0 N HCl has the formula: $(MoOCl_2)_2(C_9H_6NS)_2$. In a weakly acid medium (up to 1 N HCl) the compound $(MoO_2)_2(C_9H_6NS)_2$ is formed.

SUMMARY

The stoichiometric coefficients of the reaction between molybdenum and thiooxine have been determined by optical and potentiometric methods. The partition coefficient of molybdenum thiooxinate has been determined, and $K_{\text{instab.}}$ of the compound formed in toluene established.

The value of $K_{\text{instab.}}$ does not depend on the acidity over the acidity range studied, 1.15 N to 3.25 N HCl.

The value of $K_{\text{instab.}}$ was found to be 7.8×10^{-4}.

On the basis of published information and of the authors' own research work it is suggested that the compounds formed between molybdenum and thiooxine have the following compositions: in a weakly acid medium $(MoOCl_2)_2(C_9H_6NS)_2$ and in a strongly acid medium $(MoO_2)_2(C_9H_6NS)_2$.

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AMPEROMETRIC TITRATION OF VANDIUM AND URANIUM WITH TRIVALENT TITANIUM SALTS

Z. A. Gallai and N. M. Sheina

M. V. Lomonosov Moscow State University

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The use of compounds of certain elements in their lower valence states as reagents permits determination of elements in complex mixtures in certain cases. The use of trivalent titanium salts for the determination of some oxidizing agents in the presence of appreciable amounts of quadrivalent titanium would appear to hold promise. Solutions of trivalent titanium salts have been used in visual methods of volumetric analysis for the determination of iron [1], iodates [2] and chlorates [3], while they have been used in potentiometric methods for the determination of copper, mercury, bismuth, gold, ruthenium, osmium, molybdenum, and selenium.

Trivalent titanium compounds have not been used as reagents in amperometric titration. We established earlier [4] that titanium is oxidized on a rotating platinum microelectrode, and that at a potential of 0.4-0.9 v, the diffusion current is proportional to titanium concentration. This valuable property of trivalent titanium salts can be used for the amperometric titration of a number of oxidizing agents using anodic polarization of a platinum microelectrode. Since trivalent titanium is a fairly strong reducing agent ($E_0 Ti_{IV}/Ti_{II}$ = -0.04 v), we thought it would be interesting to use it as a titrant for determining sexivalent uranium ($E_0 UO_2^{2+}/U^{IV}$= +0.407 v) and vanadium in its quadri- and quinquevalent states, in pure salts and in the presence of quadrivalent titanium.

All the work was carried out on a visual type polarograph (Geologopribor) fitted with a M-21 galvanometer (maximum sensitivity 2.4×10^{-9} amp/mm/m). The indicator electrode was the usual type of rotating platinum microelectrode (5 mm long) while the reference electrode was a saturated calomel half-element. The solution was prepared by appropriate dilution of 15% commercial $TiCl_3$ solution with acids (either HCl 1:1 or 4 N H_2SO_4). The solutions were stored in dark glass bottles [5]. Since trivalent titanium compounds are readily oxidized in air, the reagent was stored under purified nitrogen and all experiments were carried out under purified nitrogen. The concentration of the working solution was checked potentiometrically or amperometrically against standard potassium dichromate [4]. The solution was stable for three weeks.

Titration of Quinque- and Quadrivalent Vanadium. Depending on the conditions, quinquevalent vanadium compounds are reduced by trivalent titanium to the quadri- or trivalent state (in the latter case reduction does not always proceed quantitatively).

Quinquevalent vanadium is quantitatively reduced to the trivalent state in a supporting electrolyte of H_2SO_4 starting at a concentration of 0.5 N. In a supporting electrolyte of 0.1 M sodium tartrate (pH 5.9) vanadium is only reduced to the quadrivalent state. In a supporting electrolyte of hydrochloric acid of different concentrations quinquevalent vanadium is reduced in a different way from that in which it is reduced in sulfuric acid, because of the formation of chloride complexes of quadrivalent vanadium [6]. Reduction proceeds to the quadrivalent state (the error is, however, 6%).

We thought it would be interesting to study the reduction of V^{IV} with trivalent titanium. All the experiments were carried out with $VOSO_4$ which was prepared by reducing a standard solution of ammonium vandate with sulfur dioxide. Titration was carried out at a potential of 0.8 v using the oxidation current of titanium. The reaction between the materials indicated was studied amperometrically in various supporting electrolytes. As a result the following facts emerged: reduction does not occur in a supporting electrolyte of hydrochloric acid or in 0.1 M sodium tartrate (pH 5.9), while in a sulfuric acid supporting electrolyte V^{IV} is reduced to V^{III}, the reduction going furthest in 10 N H_2SO_4. In the latter instance the error in determining 0.7-0.9 mg V does not exceed 2%.

From the results obtained (Table 1) it follows that solutions of trivalent titanium can be used for amperometric titration of quadrivalent vanadium, not only in pure salts, but in the presence of appreciable amounts of Cr^{III}, Mn^{II}, and Ti^{IV} in a supporting electrolyte of 10 N H_2SO_4.

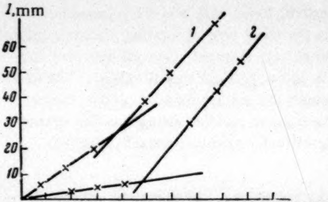
TABLE 1. Determination of Vanadium in a Supporting Electrolyte of 10 N H_2SO_4 in the Presence of Foreign Elements

Foreign elements	V, mg		Error, %	Foreign elements	V, mg		Error, %
	taken	found			taken	found	
—	0,46	0,45	—2,0	Ti^{IV} —100	0,68	0,63	—7,0
—	1,39	1,38	—0,7	60	2,00	2,06	3,0
Cr^{3+} 10	0,92	0,91	—1,0	— 60	1,00	1,02	2,0
—100	0,92	0,89	—3,0	—104	1,00	1,04	4,0
Mn^{2+} 50	0,68	0,67	—1,4				

Titration of Sexivalent Uranium. The majority of titrimetric methods of determining uranium are based on its reduction to the quadrivalent state with subsequent titration by some strong oxidizing agent. Earlier, we developed an amperometric method for titrating sexivalent uranium with divalent chromiun salts [7]. This method, however, is only applicable in the presence of approximately equal amounts of uranium (VI) and titanium (IV).

For our work we prepared a solution of uranyl nitrate in sulfuric acid; it was standardized by the ammonia method (5.037 mg U in 1 ml).

Quadrivalent uranium compounds are oxidized under conditions of anodic polarization of a platinum electrode; in a supporting electrolyte of 1 N H_2SO_4 oxidation starts at a potential of approximately 0.5 v. This essentially affects the shape of the titration curve (diagram, curve 1). At room temperature in a supporting electrolyte of sulfuric acid (1-10 N) and hydrochloric acid (1-8 N), titration results are always low, and the error for uranium is very high. Experimental results improve on taking the galvanometer readings three minutes after each addition of reagent (supporting electrolyte 10 N H_2SO_4, curve 2). This, however, appreciably lengthens the time taken for titration. At a solution temperature of about 70° readings can be made after 30 sec. All this indicates that sexivalent uranium is reduced slowly by trivalent titanium.



Titration of quadrivalent uranium with $TiCl_3$ solution in a supporting electrolyte of 10 N H_2SO_4. 1) Galvanometer readings taken after 1 min; 2) readings taken after 3 min.

We studied the effect of traces of Fe^{2+}, Cu^{2+}, and Sn^{2+} on speeding up the reaction. It was found that addition of small amounts of $SnCl_2$ (one drop of a 1% solution) to 10 ml of test solution appreciably speeds up the reaction. This means that uranium can be titrated more quickly, while the experimental error in determining 3-6 mg uranium does not exceed 1%. Pyrophosphoric acid proved even more effective. E. P. Nikolaeva and Yu. M. Shchekochikhin established that addition of pyrophosphoric acid increases $E_{U^{VI}/U^{IV}}$ from 0.4 to 0.6 v. Moreover, it is known that pyrophosphoric acid gives a complex compound with quadrivalent titanium, which, in turn, lowers the redox potential of the system Ti^{IV}/Ti^{III}.

Thus the introduction of this reagent essentially increases the difference in potentials of the reactants. It was established that introduction of pyrophosphoric acid (0.2-0.3 ml of 50% $H_4P_2O_7$) to a supporting electrolyte of 1 N H_2SO_4 permits titration at E = 0.8 v, and, since quadrivalent uranium is not oxidized in the presence of $H_4P_2O_7$, the titration curve has a sharper break. Titration can be carried out taking the galvanometer readings after 30 sec. The error in determining 3-10 mg of uranium does not exceed 1.3%.

Solutions of trivalent titanium permit determination of uranium in the presence of appreciable amounts of quadrivalent titanium (Table 2) when the solution being titrated contains pyrophosphoric acid. Titration in a supporting electrolyte of 1 N H_2SO_4 to which $H_4P_2O_7$ has been added permitted uranium to be determined in the presence of 100 times its amount of titanium, the galvanometer readings being taken 30 sec after addition of titrant.

TABLE 2. Titration of Sexivalent Uranium in the Presence of Quadrivalent Titanium in a Supporting Electrolyte of 1 N H_2SO_4 + $H_4P_2O_7$ (1 ml of 50% $H_4P_2O_7$ in 10 ml solution)

Ti introduced, mg	U, mg		Error, %	Ti introduced, mg	U, mg		Error, %
	Taken	Found			Taken	Found	
—	3,02	3,01	0,3	50	5,04	5,07	0,7
—	5,04	4,96	1,3	15	3,02	3,05	1,0
—	10,08	10,05	0,5	300	3,02	3,08	2,6
5	5,04	5,01	0,5				

SUMMARY

An amperometric method has been developed for titrating quadrivalent vanadium with trivalent titanium in pure salts and in the presence of chromium, manganese, and titanium. Conditions have been established for amperometric titration of uranium with trivalent titanium in the presence of quadrivalent titanium up to a ratio of U:Ti = 1:100.

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QUANTITATIVE DETERMINATION OF URANIUM IN ORES BY AN OSCILLOGRAPHIC POLAROGRAPHIC METHOD

D. I. Ryabchikov, Ya. P. Gokhshtein, and Kao Ts'ai Sheng

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Several papers have been devoted to the polarographic determination of uranium [1-12]. Nevertheless, many of the published methods involve separation of uranium from a number of accompanying elements and do not satisfy practical requirements.

In order to establish the possibility of determining uranium in ores without separating it from accompanying elements, we used oscillographic polarography. Different methods are used for bringing the ore into solution, depending on the content of uranium, silica, and accompanying elements in the ore. Most uranium ores decomposed with nitric acid to which hydrochloric acid is added in some cases. Ores containing appreciable amounts of silica are treated with a mixture of hydrofluoric and hydrochloric acids [13]. Carbonate ores are decomposed with a mixture of HF and H_2SO_4 or with a mixture of HF and HNO_3. Titanium-niobium ores are fused with a large amount of $K_2S_2O_7$ and the melt dissolved in phosphoric acid. The composition of the supporting electrolyte for polarographing uranium depends on the method used for decomposing the ore.

The reduction and oxidation mechanisms of the products formed during electrolysis of uranyl ions in various media have been studied in fair detail [14-17].

Measurements were made on a GEOKhI Mark 2M oscillographic polarograph [18]. The cell consisted of a dropping mercury electrode and a saturated calomel electrode. The mercury was carefully purified and distilled twice in vacuo. The peak potentials φ_p on the oscillograms were found by a method described earlier [19]; their values are given relative to the saturated calomel electrode (sce). The potential of the dropping electrode (φ) was determined by including a second auxiliary electrode (sce) in the circuit, while the instantaneous potential difference $\varphi_{cathode} - \varphi_{auxiliary}$ was measured by means of a setup specially constructed for measurement of equilibrium emf's [20]. In acid solutions dissolved oxygen does not affect the maximum current of UO_2^{2+}; accordingly uranium was determined quantitatively without removal of oxygen.

Standard solutions were prepared by dissolving chemically pure uranyl acetate in water. The test solutions were made up in twice distilled water.

Uranium was determined in titanium-niobium and carbonate ores, and also in ores containing large amounts of phosphorus and iron.

Establishment of Optimum Conditions for Determining Uranium in Ores. The titanium-niobium ore dissolved readily in concentrated (anhydrous) phosphoric acid on heating. After dissolution of an aliquot, the solution acquired a green color which indicated that it contained mainly quadrivalent uranium. The light absorption maxima at 420, 480, 540, and 660 mμ are characterisitic of U^{IV} [21].

U^{IV} was oxidized to U^{VI} by addition of $K_2S_2O_8$ on heating. At the same time, during this stage, lead was precipitated from solution as $PbSO_4$ so that interference of large amounts of Pb^{2+} on the UO_2^{2+} peak was eliminated. Uranium was determined in this case in a supporting electrolyte of 1 M H_3PO_4 + 0.25 M K_2SO_4 [16]. In 1 M H_3PO_4 + 0.25 M K_2SO_4, UO_2^{2+} ions are reduced in one step [16]. Only one cathodic wave for uranium caused by reduction of U^{VI} to the quadrivalent state appeared on the current-voltage curve. Reduction is irreversible. In a phosphoric acid solution the current of the uranyl ions is directly proportional to their concentration. No anodic curve for uranium was detected in 1 M H_3PO_4 + 0.25 M K_2SO_4 [16].

It is clear from Table 1 that a number of accompanying elements do not interfere with uranium determination, since their peak potentials in phosphoric acid media are much more negative than E_p for UO_2^{2+}

TABLE 1. Effect of Accompanying Elements on I_p for UO_2^{2+} in 1 M H_3PO_4 + 0.25 M K_2SO_4

Accompanying elements, mg/ml		U taken, mg/ml	U found, mg/ml	Accompanying elements, mg/ml		U taken, mg/ml	U found, mg/ml
Fe^{3+}	0.24	0.12	0.12	Cu^{2+}	0.03	0.12	0.116
	0.60	0.12	0.12		0.06	0.12	0.088
	1.20	0.12	0.12	Pb^{2+}	0.12	0.12	0.12
Ti^{IV}	0.24	0.12	0.112	Nb^V, Ta, rare earths			
	0.60	0.12	0.117	1.20 each		0.12	0.12
	1.20	0.12	0.115				

The phosphoric acid concentration should not exceed 1 M. At higher phosphoric acid concentrations the titanium peak is shifted toward the positive side and almost fuses with the uranium wave. The sulfate ion concentration of the test solution should not exceed 0.25 M. At higher SO_4^{2-} concentrations the straight line relation between I_p and UO_2^{2+} concentration breaks down.

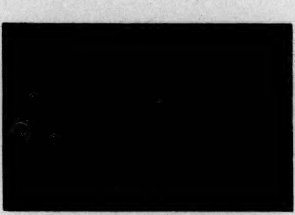

Fig. 1. Oscillogram of a phosphoric acid solution of a titanium-niobium-tantalum ore to which a standard solution of a UO_2^{2+} salt has been added. $U_= = +0.17$ v; $U_\sim = 0.95$ v; V = 1,3 v/sec. Cathodic polarization.

Fig. 2. Oscillograms of a phosphoric acid solution of a titanium-niobium-tantalum ore with five additions of a standard solution of a UO_2^{2+} salt. $U_= = +0.17$ v; $U_\sim = 0.95$ v; V = 1.3 v/sec. Cathodic polarization.

An oscillogram of a phosphoric acid solution of a titanium-niobium-tantalum ore to which a standard solution of an uranyl salt has been added is shown in Fig. 1. A constant voltage $U_= = +0.17$ v and a saw-toothed negative potential $U_\sim = 0.95$ v were applied to the cell. The highest negative potential was -0.780 v. The rate of potential change was 1.3 v/sec, while a single sweep with a delay of 13 sec after the previous drop had broken off was used. The current of the supporting electrolyte—1 M H_3PO_4 + 0.25 M K_2SO_4—, the first curve from the bottom, is compared with the current of a solution containing test ore, the second from the bottom, in Fig. 1. The third curve is that of the UO_2^{2+} current after adding 0.235 mg of U to the test solution. The volume of the solution before addition of the standard solution was 3 ml. The bottom straight line is the zero line. The current for uranium is directly proportional to its concentration so that the the U content of the ore can be calculated by the method of additions (Fig.2). Fig. 2 was obtained under the same conditions as those used for Fig. 1. On this oscillogram the first curve from the bottom corresponds to the cutrent for the supporting electrolyte 1 M H_3PO_4 + 0.25 M K_2SO_4. The second curve corresponds to the current of the solution containing the ore. The current-voltage curves 3, 4, 5, 6, and 7 were obtained after addition of successive portions of 0.1 ml of a standard uranyl salt solution to 3 ml of a phosphoric acid solution of the ore.

The straight line is the zero line (1 ml of standard solution contained 2.356 mg U).

Direct dissolution of ore in phosphoric acid followed by polarographic determination of uranium in this medium without preliminary chemical preparation appreciably speeds up determination. Nevertheless, because of the low solubility of the ore in concentrated H_3PO_4 (not more than 0.05 g in 1 ml) it was impossible, using the maximum sensitivity of the oscillographic polarograph, to determine less than 2% U in ores. The current of the supporting electrolyte, which fuses with the current of a solution containing very small amounts of uranium on the oscillogram, prevents one increasing the sensitivity.

In order to overcome this difficulty we increased the weight of aliquots of ore poor in uranium and decomposed them by fusion with $K_2S_2O_7$ [22]. The melt was dissolved in phosphoric acid and the uranium determined in a supporting electrolyte of 1 M H_3PO_4 + 0.25 M K_2SO_4. Ore poor in uranium was also decomposed by treating it with HF, removing F^- ions with nitric acid and determining the uranium in a supporting electrolyte of 1 N HNO_3.

Cathodic polarization of the electrode in a nitric acid solution of UO_2^{2+} gives only one cathodic wave on the current-voltage curve. Such a cathodic wave for UO_2^{2+} shown in Fig. 3 ($U_{=}$ = +0.08 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec). A single sweep with a 13 sec delay after the previous drop had broken off was applied to the cell. The straight line is the zero line; the upper curve corresponds to the current for a solution containing 0.046 mg U/ml. The maximum current of UO_2^{2+} was measured from the supporting electrolyte curve to the maximum. For very low uranium contents in 1 N HNO_3 the current for the solution differs little from the current of the supporting electrolyte, so that the sensitivity with which uranium can be determined cannot be increased. Nevertheless, anodic polarization in the case of a nitric acid solution of an uranyl salt almost excludes the effect of the supporting electrolyte current on the peak of quinquevalent uranium (Fig. 4). The anodic curve of U in 1 N HNO_3 containing 4.6×10^{-2} mg U/ml is shown in the oscillogram in Fig. 4. Fig. 4 was obtained for $U_{=}$ = -0.5 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec and for a single impulse with a delay of 13 sec after the previous drop had broken off. The sweep voltage was varied from -0.5 to +0.45 v. The middle curve – the current of the supporting electrolyte 1 N HNO_3 – intersects the zero line, and, at the more negative potentials, lies below the zero line. The upper uranium curve intersects the supporting electrolyte curve at φ = -0.25 v while that part of the curve which lies below the line of the supporting electrolyte is caused by reduction of UO_2^{2+} to UO_2^{+}. Since at the peak potential of the anodic wave (ϕ_p = -0.15 v) the supporting electrolyte current coincides with the zero line, the anodic current was measured from the zero line to the maximum. The cathodic current was measured from the intersection point of the supporting electrolyte current with the zero line to the break in the wave located below the supporting electrolyte current. The current of the uranium anodic wave is equal to the sum of the cathodic and anodic currents measured in this way. The oscillogram in Fig. 4 znd Table 2 show that in the case of a nitric acid solution of a UO_2^{2+} salt, anodic polarization allows one to determine low concentrations of uranium in 1 N HNO_3 at the maximum sensitivity of the apparatus.

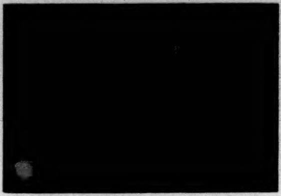

Fig. 3. Oscillogram for the cathodic wave of UO_2^{2+} in 1 N HNO_3. $U_{=}$ = +0.08 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec.

Fig. 4. Anodic wave. U_V in 1 N HNO_3. $U_{=}$ = -0.5 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec. U_{sweep} varied from -0.5 to +0.45 v.

The results given in Table 2 show that the value of the anodic peak of uranium is directly proportional to its concentration. The sensitivity of the method is 3×10^{-3} mg/ml.

The effect of accompanying elements on the value of the anodic peak of uranium was also studied in a nitric acid medium. It was established that most elements do not interfere with determination of uranium. The exception is trivalent iron which exhibits a strong influence on the maximum current of the anodic wave when its content in the solution is five times the uranium concentration.

TABLE 2. Relation between the Maximum Current of the Anodic Wave of Uranium and its Concentration in 1 N HNO_3. $U_{=}$ = -0.5 v; $U_{\sim}$ = 0.95 v; V = 1.3 v/sec. Single sweep. 13 sec delay after drop has broken off.

U, mg/ml	I_p, μa	U, mg/ml	I_p, μa
0,245	7,38	0,023	0,69
0,169	5,06	0,012	0,36
0,092	2,78	0,006	0,18
0,068	2,03	0,003	0,09
0,046	1,37		

The 1 N HNO_3 solution is suitable for determination of uranium in those ores which have been decomposed beforehand with a mixture of hydrofluoric and hydrochloric acids or with HF + HNO_3 (usually ores containing appreciable amounts of silica dissolve in a mixture of HF and HCl or HF and HNO_3). An ore containing a large amount of iron (about 70%) was decomposed with a mixture of HF and H_2SO_4; after removal of F^- and dissolving the residue in 0.1 N H_2SO_4, uranium was determined on the basis of the first cathodic wave [17]. Interference from Fe^{3+} was eliminated by addition of hydrazine sulfate. The oscillogram of

the ore containing appreciable amounts of iron, with two additions of standard solution of uranyl is shown in Fig. 5. The oscillogram was obtained during cathodic polarization using a single sweep and a 13 sec delay after the previous drop had broken off. $U_= = +0.02$ v and $U_\sim = 0.95$ v were applied to the cell; the rate of change in voltage was $V = 1.3$ v/sec. The sweep voltage was varied from +0.02 to -0.93 v. The first curve from the bottom corresponds to the current of the supporting electrolyte—0.1 N H_2SO_4; the second, to the solution of the test ore; while the third and fourth waves correspond to a solution of the same ore with additions of standard uranium solution corresponding to 0.235 and 0.470 mg U/ml. The initial volume of the solution was 3 ml. It is clear from Fig. 5 that the maximum current of the uranyl ions in the 0.1 N H_2SO_4 containing the uranium from the ore is directly proportional to its concentration.

Fig. 5. Oscillogram of a sulfuric acid solution of an ore containing an appreciable iron content, to which two portions of a standard uranium solution have been added. The first cathodic wave of UO_2^{2+} ions was used. $U_= = +0.02$ v; $U_\sim = 0.95$ v; $V = 1.3$ v/sec.

Thus oscillographic polarography permits quantitative determination of uranium in some ores without preliminary separation of accompanying elements.

Experimental Procedure. Titanium-niobium-tantalum ores and also other ores soluble in concentrated phosphoric acid are analyzed as follows. 0.1-0.3 g of finely ground sample is dissolved on heating in 7 ml of H_3PO_4 (85%) contained in a 50-100 ml beaker. After dissolution is complete the solution has a green color; it is cooled and diluted 2-3 times with distilled water. After adding 3 g of $K_2S_2O_8$ the contents of the beaker are heated until the green color has disappeared and boiling is then continued for a further 3-5 min. After cooling, the solution is transferred to a 100 ml standard flask, diluted to the mark with water and carefully mixed. Three ml of this solution is transferred to the electrolyzer and an oscillogram taken at $U_= = +0.17$ v and a negative saw-tooth voltage of -0.95 v. A single sweep with a 13 sec delay after the previous drop has broken off is applied to the cell. One determination takes less than one hour.

A titanium-niobium-tantalum ore containing less than 2% of uranium can be dissolved by fusing it with $K_2S_2O_7$ For this purpose a 1-2 g aliquot of ore is fused in a platinum or porcelain crucible with 6 g of $K_2S_2O_7$ for 30 min at 400-600°. The melt is leached with water on heating in a beaker, the solution is transferred to a 100 ml standard

TABLE 3. Determination of Uranium in Ores

Ore	Method used for decomposing the ore	Medium for uranium determination	Uranium found, %			
			by the method suggested*	chemically	radiometrically	x-ray spectrographically
Titanium-niobium-tantalum ore	Dissolved directly in H_3PO_4	1 M H_3PO_4+0.25 M K_2SO_4	11.40	10.50	11.36	11.50
			11.40			
			11.40			
			11.28			
Titanium-niobium-tantalum ore	Fusion with $K_2S_2O_7$	1 M H_3PO_4+0.25 M K_2SO_4	11.13	10.50	11.36	11.50
			11.30			
			11.44			
			11.34			
Titanium-niobium-tantalum ore	HF + HNO_3	1 N HNO_3	11.46	10.50	11.36	11.50
Carbonate ore	Fusion with $K_2S_2O_7$	1 M H_3PO_4+0.25 M K_2SO_4	0.073	0.070	—	—
Carbonate ore	HF + H_2SO_4	0.1 N H_2SO_4	0.069	0.070	—	—
Carbonate ore	HF + HNO_3	1 N HNO_3	0.072	0.070	—	—
Ore with high phosphorus content	Fusion with $K_2S_2O_7$	1 M H_3PO_4+0.25 M K_2SO_4	0.165	0.170	—	—
	HF + H_2SO_4	0.1 N H_2SO_4	0.174	0.170	—	—
Ore with high iron content	HF + H_2SO_4	0.1 N H_2SO_4	0.204	0.200	—	—
			0.201			
			0.207			

flask and 6-7 ml of 85% H_3PO_4 added; the volume is then made up to the mark with water. Three ml of this solution is transferred to the electrolyzer and an oscillogram is taken under the same conditions as those used when the ore is dissolved directly in concentrated H_3PO_4. One determination takes about two hours. When ores are decomposed with a mixture of HF and HCl or with HF + HNO_3 the residue is dissolved in 1 N HNO_3. Three ml of the solution obtained is introduced into the electrolyzer and anodic polarization carried out. $U_= = -0.5$ v and a positive saw tooth voltage $U_\sim = 0.95$ v are applied to the cell. An oscillogram of the anodic wave of uranium is obtained on the screen of the oscillographic polarograph using a single sweep and a delay of 10-13 sec after the previous drop has broken off.

Carbonate and phosphate ores low in uranium, and ores containing large amounts of iron can be analyzed as follows.

A 1-2 g aliquot of ore is placed in a platinum basin, and 10 ml of 40% HF and 6 ml of H_2SO_4 (sp.gr. 1.84) added. The contents are heated and then evaporated to dryness. Decomposition of the ore with the HF and H_2SO_4 mixture is repeated three times. The residue is cooled and then dissolved in 20-30 ml of 0.1 N H_2SO_4. Three g of hydrazine sulfate is added and the solution boiled for several minutes. The solution is cooled and transferred to a 50 ml standard flask. The volume of the solution is made up to the mark with 0.1 N H_2SO_4. Three ml of the solution obtained is introduced into an electrolyzer and oscillograms taken at $U_= = +0.02$ v and $U_\sim = 0.95$ v, using a single sweep with a delay time of 10-13 sec after the previous drop has broken off.

Whatever ore is analyzed the oscillograms of the supporting electrolyte, test solution, and solution to which a standard solution of uranium has been added are recopied on tracing paper, after which, using the usual method [19] the points are measured and the uranium content calculated by the method of additions. Results of determinations carried out by four methods are compared in Table 3; the methods used included the suggested method, Volkov's titrimetric method [23], radiometric, and x-ray spectrographic method [24].

The results in Table 3 show that oscillographic polarography permits determination of uranium in certain ores without preliminary removal of accompanying elements.

SUMMARY

It has been shown that oscillographic polarography is suitable for the determination of uranium in certain ores without preliminary removal of accompanying elements.

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SUCCESSIVE EXTRACTION PHOTOMETRIC DETERMINATION OF TRACES OF COPPER, NICKEL, IRON, AND MANGANESE

A. B. Blank, A. M. Bulgakova, and N. T. Sizonenko

All-Union Scientific-Research Institute of Monocrystals,
Scintillators, and Highly Pure Materials, Khar'kov

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Iron, copper, nickel, and manganese are widely spread impurities which are introduced into finished products from raw materials and constructional materials. The necessity of determining the content of these elements is determined by the fact that in the presence of microgram amounts of them the useful properties of many materials, e.g., those used in the production of scintillators and luminophors [1], deteriorate appreciably.

In the method which we should like to propose, copper, nickel, divalent iron, and manganese are extracted in succession from an ammoniacal-citrate buffer solution with diethyldithiocarbamate, dimethylglyoxime, 1-nitrose-2-naphthol, and diethyldithiocarbamate respectively.

The sensitivity of the reactions used is characterized by the data given in Table 1; the value of $\bar{\varepsilon}$ changes slightly on switching from one apparatus to another.

TABLE 1. Photometric Characteristics of the Complexes Used for Determination of Copper, Nickel, Iron, and Manganese

Compound	Molar extinction coefficient			"Mean" molar extinction coefficient (for the FEK-M apparatus)	
	λ, mμ	$\varepsilon \times 10^{-3}$	cited reference	FEK-M filter	$\bar{\varepsilon} \times 10^{-3}$
Copper diethyldithiocarbamate	436	12.8	[2]	blue	6.9
Compound of nickel with dimethylglyoxime in the presence of oxidizing agent	442	11.6	[3]	blue	8.8
Ferrous nitrosonaphtholate	690	16.0	[4]	red	12.0
Manganese diethyldithiocarbamate	400	3.8	[5]	blue	3.4

Copper ions are extracted with a solution of lead diethyldithiocarbamate in chloroform [6,7]. Only Ag^+, Hg^{2+}, Bi^{3+}, and Tl^{3+} interfere (the limiting ratios for 1 μg copper and for a maximum error of 20% are 1:500; 1:500; 1:4; and 1:10 respectively).

Nickel is separated by extraction of its complex with dimethylglyoxime with chloroform, followed by its transference to the aqueous phase and determination with dimethylglyoxime in the presence of an oxidizing agent [8]. Since copper has been removed beforehand there is no need to destroy the complex of copper with dimethylglyoxime.

Iron is separated and determined by means of the extraction photometric reaction of Fe^{2+} with 1-nitroso-2-naphthol which we had studied earlier [4] and which has a fairly high sensitivity. Apart from copper and nickel, of the usual metal ions only Co^{2+} and Ag^+ interfere with determination of iron (the limiting ratios for 5 μg ions are 1:4 and 1:10 for cobalt and silver respectively).

After removal of copper, nickel, and iron, only Co^{2+} and MoO_4^{2-}, which also form colored complexes, interfere with the determination of manganese in the form of its compound with diethyldithiocarbamate [9].

The order of separation adopted permits iron and manganese to be determined in the presence of 20 times their amount of MoO_4^{2-} and 10 times their amount of Co^{2+}.

Reagents, Solutions, and Measurement Technique. Solution of Lead Diethyldithiocarbamate in Chloroform. An aqueous solution containing 0.20 g of sodium diethyldithiocarbamate, 0.20 g lead nitrate, and 1 g sodium potassium tartrate is neutralized with ammonia to the phenol red color and shaken with chloroform. After being washed twice with two portions of water the extract is filtered and then diluted with chloroform to one liter.

Sodium diethyldithiocarbamate is purified by precipitating it from a saturated ethanolic solution with excess diethyl ether, after which it is dried in air [10].

Bromine water is prepared from analytical grade bromine purified by distillation.

Dimethylglyoxime (analytical grade), trisodium citrate (analytical grade), hydrochloric and sulfuric acids (chemically pure grade), perchloric acid (specially pure grade) were used. The remaining reagents and solutions were the same as those described in [4].

Metal salts were recrystallized; their solutions were acidified with sulfuric acid. The concentrations of the stock solutions of copper, nickel, and ferric sulfates, and manganese chloride containing 1000 μg of the metal per ml, were checked by titrimetric methods [11-13].

The optical density was measured on a FEK-M photoelectric-colorimeter relative to the solutions obtained in the control tests; the final volume was 24 ml in each case, a cuvette with a path length of 5 cm was used. The experimental results were treated statistically [14] at a confidence level of 0.95.

Experimental Procedure. An aliquot of preparation or preliminarily processed material is dissolved in water, to which is added 5 ml of an ammoniacal-citrate buffer solution (4% solution of trisodium citrate containing 5 ml of 0.1% phenol red per liter and neutralized with ammonia to the end point of this indicator) and if necessary, additionally neutralized with ammonia*. The solution is transferred to a 250 ml separating funnel and diluted to approximately 50 ml with water.

Determination of Copper. Copper is extracted twice with the solution of lead diethyldithiocarbamate in chloroform (5 ml portions), after which the solution is washed with 5 ml of chloroform and the washings combined with the extract. After diution with chloroform in a standard flask, the solution is filtered into the cuvette and the optical density measured using a blue filter.

Determination of Nickel. To the solution remaining after removal of copper is added 1-2 drops of ammonia (1:20), if necessary, until the appearance of the violet color of the indicator (pH ≥ 8.0). This is followed by 1 ml of dimethylglyoxime solution (1% solution in distilled aqueous alcohol); after 15 min the complex of divalent nickel with dimethylglyoxime is extracted with three portions of 5 ml each of chloroform. The combined extracts are shaken with three lots of 5 ml each of hydrochloric acid (0.5 N). 0.2 ml of bromine water, 1 ml of ammonia sp.gr. 0.91, and 0.5 ml of dimethylglyoxime solution are added to the hydrochloric acid solution obtained which has been placed in a standard flask, the volume of the solution is made up to the mark with water and the optical density measured after 15 min using a blue filter.

Determination of Iron. Fifteen ml of ascorbic acid (10% aqueous solution) is added to the solution remaining after removal of nickel, the solution is carefully neutralized with ammonia using phenol red as indicator, 5 ml of 1-nitroso-2-naphthol solution (1 g/liter to which 120 ml of 0.1 N KOH has been added per liter) is added and the volume made up to about 150 ml with water. After 45 min the complex of iron with 1-nitroso-2-naphthol is extracted twice with isoamyl alcohol (15 and 10 ml). The combined extracts are diluted with isoamyl alcohol in a standard flask and the optical density measured using a red filter.

Determination of Manganese. After removal of iron the solution is extracted with 10 ml of chloroform in order to remove any residual isoamyl alcohol. The chloroform layer is discarded, 5 ml of sodium diethyldithiocarbamate (5% aqueous solution) is introduced into the separating funnel and the whole shaken with 5 ml of chloroform. This last operation is repeated once again after which the solution is washed with a further 5 ml of chloroform. After dilution with chloroform in a standard flask the combined extracts are filtered into the cuvette and the optical density measured 15 minutes after mixing, a blue filter being used.

Calibration Curve. Calibration curves for the determination of copper, iron, and manganese were constructed by carrying out extraction of each metal ion from an ammoniacal-citrate buffer solution, following the procedures outlined above. The calibration curve for nickel was constructed by adding known amounts of Ni^{2+} to 15 ml of 0.5 N hydrochloric acid with subsequent addition of bromine water, ammonia, and dimethylglyoxime.

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* The color transition range for phenol red is 6.8-8.0 pH units [15]; in practice, on careful neutralization with dilute ammonia (1:20) a pH value of 7.5 ± 0.5 is obtained under the conditions adopted.

All four elements were found to conform quite well to Beer's law over the concentration range studied (from 0 to 20 μg of metal in 25 ml solution). The parameters of the calibration lines calculated by the method of least squares [14, 16] are given in Table 2.

TABLE 2. Parameters of the Calibration Lines: $D = \alpha + \beta C$ (C in γ/μg)

Metal determined	No. of experiments	$\alpha \cdot 10^3$	$\beta \cdot 10^2$
Cu	38	3.3±0.6	2.177 ± 0.006
Ni	33	4.1±0.4	3.010 ± 0.004
Fe	29	–	4.292 ± 0.007
Mn	30	–	1.247 ± 0.005

TABLE 3. Determination of Cu, Ni, Fe, and Mn in the Presence of Co^{2+} (50 μg) and MoO_4^{2-} (100 μg) (5 μg each of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} added). Number of experiments n = 3.

Test element	μg found in the presence of	
	Co^{2+}	MoO_4^{2-}
Cu	5.04 ± 0.32	4.96 ± 0.54
Ni	4.90 ± 0.25	4.93 ± 0.14
Fe	5.10 ± 0.25	5.13 ± 0.38
Mn	5.35 ± 0.81	5.00 ± 0.55

Effect of Foreign Ions. The number of metal ions which interfere with the determination of copper, nickel, iron, and manganese is very small. We though it would be interesting to acquire some quantitative results on the effect of Co^{2+} and MoO_4^{2-} on the results of the determinations of iron and manganese by this method. As the results in Table 3 show, relatively large amounts of these ions do not interfere with determination of the four elements in one aliquot.

Determination of Cu, Ni, Fe, and Mn in Alkali Metal Halides. The suggested method has been tried out on solutions containing known amounts of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} (up to 20 μg of each metal) and ammoniacal citrate medium. The results obtained are given in Table 4.

Analysis of potassium chloride and bromide for impurities can be carried out directly on an aqueous solution of the preparation, while in the case of sodium iodide and ammonium fluoride these salts must be converted into sulfate or perchlorate.

An aliquot of test material is placed in a 50-70 ml crucible (5 g NaI in a quartz crucible, 3 g NH_4F in a platinum crucible with a lid), and 5 ml of sulfuric acid in the case of NaI and 10 ml of perchloric acid in the case of NH_4F added. The crucible is heated on an electric hotplate with a power of 800-1000 watts, the heating element of the hotplate being covered with a piece of asbestos paper*. The same amount of acid is added to another crucible to serve as a control. The contents of the crucible are periodically shaken, the crucible being held on its outside with crucible tongs**. After evaporation of the iodine during decomposition of NaI, the acid in the crucible is evaporated further for 10-15 min. During decomposition of NH_4F, heating is continued for 40-50 min after perchloric acid vapors have started to come off.

The contents of the cooled crucible are dissolved in water, a drop of phenol red solution is added, followed by 5 ml of ammoniacal-citrate buffer solution and the whole carefully neutralized with ammonia solution sp.gr. 0.91 until the indicator color changes from red to straw-yellow (pH approximately 2). Neutralization of the solution obtained after decomposition of ammonium fluoride is carried out in a quartz beaker. The cooled solution is transferred into a 250 ml separating funnel and diluted to approximately 50 ml with water.

During analysis of KCl and KBr, 5 g of the preparation is dissolved in water to which 5 ml of ammoniacal-citrate buffer solution has been added.

The determination is completed according to the procedure outlined above.

When it is necessary to apply a correction to the experimental results, the iron content of the ammonia is periodically determined; for this purpose 50 ml of the latter is evaporated to dryness in a quartz beaker and the residue dissolved in water containing ammoniacal-citrate buffer solution.

Results for the determination of four elements in alkali metal halides are given in Table 5. In experiments

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* A standard ceramic with a packed nichrome spiral is fixed on a ceramic base, e.g., a thick walled faced brick. A tube fitted onto a large glass funnel is fitted over the hotplate as a safeguard against dust.

** The ends of the tongs are protected with pieces of rubber tubing.

TABLE 4. Successive Determination of Cu, Ni, Fe, and Mn on one Aliquot

Metal determined / No. expt.	Cu			Ni			Fe			Mn		
	added, a_i(μg)	found x_i(μg)	$z_i=\frac{x_i}{a_i}$	a_i	x_i	z_i	a_i	x_i	z_i	a_i	x_i	z_i
1	10,0	10,52	1,052	5,26	4,51	0,857	10,0	9,60	0,960	10,0	9,78	0,978
2	—	—	—	—	—	—	10,0	9,11	0,911	5,0	5,93	1,186
3	1,0	1,06	1,060	5,26	5,68	1,080	10,0	10,21	1,021	—	—	—
4	—	—	—	5,26	5,11	0,971	—	—	—	5,0	4,41	0,882
5	1,0	0,87	0,870	5,26	6,18	1,175	10,0	9,55	0,955	5,0	5,85	1,170
6	1,0	1,01	1,010	5,26	5,45	1,036	10,0	9,55	0,955	—	—	—
7	1,0	1,24	1.240	1,05	0,80	0,762	1,0	1,33	1,330	—	—	—
8	1,0	1,01	1,010	1,05	1,04	0,990	1,0	0,93	0,930	2,0	2,57	1,285
9	1,0	1,19	1,190	1,05	0,94	0,895	1,0	1,07	1,070	2,0	2,16	1,080
10	1,0	1,19	1,190	1,05	0,97	0,924	1,0	1,00	1,000	2,0	2,32	1,160
11	10,0	10,52	1,052	10,53	10,70	1,016	10,0	9,44	0,944	10,0	9,54	0,954
12	10,0	10,47	1,047	—	—	—	10,0	9,67	0,967	10,0	9,94	0,994
13	20,0	19,48	0,974	21.06	20,29	0,963	20,0	20,04	1,002	20,0	20,21	1,011
14	20,0	19,52	0,976	21,06	20,55	0,976	20,0	19,87	0,994	20,0	19,41	0,971
15	5,0	5,01	1,002	5,26	5,30	1,008	5,0	4,87	0,974	5,0	5,13	1,026
16	10,0	10,20	1,020	10,53	10,66	1,012	10,0	9,69	0,969	10,0	9,78	0,978
No. expts. in	14			14			15			13		
z	1,050			0,976			0,999			1,052		
Dispersion $S^2 \cdot 10^3$	9,7			9,8			9,9			13,4		
Accuracy $\pm\delta_{0.95}$	0,057			0,057			0,055			0,070		
Error (relative) %	5,7			5,7			5,5			7,0		

TABLE 5. Determination of Cu, Ni, Fe, and Mn in Alkali Metal Halides Using One Aliquot (5 g of salt and 5 μg each of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} were introduced into the test sample, while the control sample contained 5 g of salt)

Preparation	No. of expts. in	Element determined	Mean arithmetic value of the values obtained	Dispersion $S^2 \cdot 10^2$	Accuracy $\pm\delta_{0.95}$	Error (relative), %
NaI	6	Cu	4,93	2,27	0,16	3,2
		Ni	4,95	3,10	0,18	3,6
		Fe	4,86	3,10	0,18	3,6
		Mn	4,88	12,43	0,37	7,4
KBr	5	Cu	5,23	7,64	0,34	6,8
		Ni	5,02	1,65	0,16	3,2
		Fe	4,99	8,19	0,35	7,0
		Mn	5,15	14,75	0,48	9,6
KCl	5	Cu	5,13	5,83	0,30	6,0
		Ni	4,93	3,44	0,23	4,6
		Fe	4,99	3,15	0,22	4,4
		Mn	4,97	1,74	0,16	3,2
NH_4F	5	Cu	5,00	0,61	0,10	2,0
		Ni	5,00	7,50	0,34	6,8
		Fe	4,88	5,70	0,30	6,0
		Mn	5,00	4,84	0,27	5.4

with NaI and NH_4F, the solution containing 5 g of the salt and measured amounts of Cu^{2+}, Ni^{2+}, Fe^{3+} and Mn^{2+} was evaporated to a minimum volume in a crucible, after which the residue was treated with H_2SO_4 or $HClO_4$. In experiments with KCl and KBr, the solution containing 5 g of the salt and measured amounts of each of the metals was introduced directly into the separating funnel. In all cases the control differed from the actual test only in that the solutions of the copper, nickel, iron, and manganese salts were replaced by the same volume of water; the control test was acidified with sulfuric acid like the test solutions.

SUMMARY

A method has been developed for the successive extraction photometric determination of traces of copper, nickel, iron, and manganese on one aliquot of high purity alkali metal halides (NaI, KBr, KCl, NH_4F, which are used for the production of scintillation and optical monocrystals.

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CHEMICO-SPECTROGRAPHIC DETERMINATION OF MICRO-IMPURITIES IN SODIUM AND POTASSIUM CHLORIDES AND IN TARTARIC ACID

G. A. Pevtsov and T. G. Manova

All-Union Scientific-Research Institute of Chemical Reagents, Moscow
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Chemico-spectrographic methods* are often used for the determination of impurities in those cases where the direct spectrographic method is not sensitive enough. Various chemico-spectrographic techniques have been described [1, 2]. The method of Solodovnik et al. [3] has been used very successfully on high purity acids.

The present article is devoted to a method based on conversion of the elements to be determined into sparingly soluble compounds, followed by precipitation of the latter on a collector and filtration of the collector from the solution. The dried collector plus impurities is then analyzed spectrographically.

In this way we** have determined tin, lead, cadmium, and bismuth present as impurities (of the order of 1×10^{-5}% each) in sodium and potassium chlorides, and also copper, cobalt, tin, lead, and silver in tartaric acid. As a basis for the determination of impurities in potassium and sodium chlorides we adopted a technique which we had developed earlier for chromic oxide, in which bismuth, tin, lead, and cadmium are coprecipitated on cupric sulfide formed on passing hydrogen sulfide into the solution [4]. Complete isolation of all the elements indicated above on the cupric sulfide was achieved by adding sodium diethyldithiocarbamate to the solution; sodium diethyldithiocarbamate has been successfully used previously both for analytical purposes [5], and also for purifying various salts from heavy metal impurities [6].

The enrichment process was carried out by different variants. Hydrochloric acid was added to the solution of sodium (or potassium) chloride (10 g in 50 ml of distilled water) containing the elements indicated above as impurities in amounts of 1×10^{-5}% each (in terms of the salt), until the pH was 3; 2.5 mg of copper as its sulfate was then added. Hydrogen sulfide was passed through the solution and 0.5 ml of a 1% aqueous solution of sodium diethyldithiocarbamate added. After two hours the cupric sulfide was filtered off through an ashless filter paper (1.5 cm diameter) on a Buchner funnel and washed with 5 ml of hydrogen sulfide water. The dry precipitate plus filter paper were burnt in an activated arc (220 v, 7.5 amps) using carbon electrodes (diameter of the cylindrical channel 4.2 mm, depth 6 mm). The spectra were photographed on an ISP-28 spectrograph fitted with a three lens slit illuminating system and a stepwise attenuator; the spectra were recorded on spectrographic photographic plates type II with a sensitivity of 16 units, using an exposure time of 2 min and a slit width of 0.015 mm.

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* The terminology relating to chemico-spectrographic analysis has not yet been finalized. In our opinion, chemico-spectrographic methods involving collectors are characterized by the following indices: 1) the theoretical enrichment coefficient, which, calculated in terms of the test element, is the ratio of the weighable amounts of test sample and collector; 2) completeness of coprecipitation of the test impurity sorbed by the collector (as a % of the total content of the impurity in the test sample); 3) the coefficient of the increase in sensitivity of the determination, which is the ratio of the sensitivity obtained during a direct spectrographic determination to that obtained during a chemico-spectrographic determination.

This last index will, of course, change according to which direct spectrographic method is taken for comparison.

** I. A. Sviridkova took an active part.

The spectra of a "blank", those of the test sample and of three standards prepared from spectrographically pure cupric sulfide were taken 2-3 times on one photographic plate.

The following lines were measured photometrically on the spectra obtained:

Bi 3067.7; Pb 2833.1;
Sn 2839.9; Cd 2288.0.

Calibration curves were constructed within the coordinates S¬log C.

TABLE 1.

Element	Content of the element in the salt, %	Amount of element found in the salt, % (mean value)	Concentration of the element in the collector, %	Experimental error (relative), %
Bismuth	$1 \cdot 10^{-5}$	$1.18 \cdot 10^{-5}$	$2.6 \cdot 10^{-2}$; $4.3 \cdot 10^{-2}$ $3.4 \cdot 10^{-2}$; $3.4 \cdot 10^{-2}$ $3.8 \cdot 10^{-2}$; $1.8 \cdot 10^{-2}$ Mean $3.2 \cdot 10^{-2}$	+18
Tin	$1 \cdot 10^{-5}$	$0.92 \cdot 10^{-5}$	$1.4 \cdot 10^{-2}$; $1.4 \cdot 10^{-2}$ $5 \cdot 10^{-2}$; $2.6 \cdot 10^{-2}$ $3.2 \cdot 10^{-2}$; $1.3 \cdot 10^{-2}$ Mean $2.5 \cdot 10^{-2}$	-8
Cadmium	$1 \cdot 10^{-5}$	$1.11 \cdot 10^{-5}$	$1.7 \cdot 10^{-2}$; $4.8 \cdot 10^{-2}$ $2.4 \cdot 10^{-2}$ Mean $3.0 \cdot 10^{-2}$	+11
Lead	$1 \cdot 10^{-5}$	$0.9 \cdot 10^{-5}$	$2.5 \cdot 10^{-2}$; $3.0 \cdot 10^{-2}$ $2.3 \cdot 10^{-2}$ Mean $2.6 \cdot 10^{-2}$	-4

Similar results were obtained when another method was used, in which the collector was spectrographically pure cupric sulfide introduced into the solution in the form of finely ground powder. In this case, after adding sodium diethyldithiocarbamate to the solution, the latter was shaken and hydrogen sulfide passed through it.

A "blank" showed the absence of the lines of test elements in the spectrum. The theoretical enrichment coefficient was 2.7×10^3 in these experiments. It follows from this that the amount of the impurities in the collector, assuming that precipitation was 100% complete, should be $1 \times 10^{-5} \cdot 2.7 \times 10^3 = 2.7 \times 10^{-2}$.

Results of determinations by this method are given in Table 1.

Calibration curves for standards prepared from CuS are shown in Fig. 1; it is clear from these that the relation between S and log C is linear.

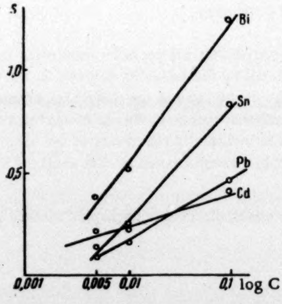

Fig. 1.

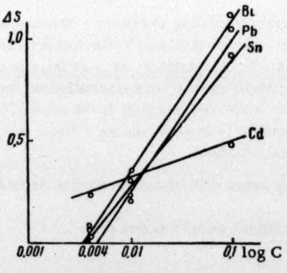

Fig. 2.

On using spectrographically pure carbon powder as collector and diethyldithiocarbamate as precipitant at pH 7.5, it was found possible to avoid the operation of passing hydrogen sulfide. On adding 0.025 g of carbon powder to a solution of NaCl or KCl under the conditions described above, such an analytical technique can only be used in those cases where the standards are prepared by enrichment from appropriate solutions of the salts with a known content of Bi, Sn, Cd, and Pb as impurities.

Under the conditions indicated above for carrying out spectrographic analysis a linear relation was obtained between $\Delta S = S_{\text{impurity}} - S_{\text{background}}$ and log C (Fig. 2) in this case. The cadmium line Cd 2265.0 was used instead of the line Cd 2288.0, since in the case of the latter the slope obtained for the curve was too small, probably, because of a self-rotation effect. This analytical variant enables one to use the "method of addition" successfully.

The sensitivity of this analytical technique is about 3.0×10^{-6}% for all the elements indicated above. At the same time, during direct determination, e.g., of Pb in sodium chloride, in an activated arc the sensitivity is 3×10^{-4}%. Thus the coefficient of the increase in the sensitivity of the determination is 1×10^{2}, while the theoretical enrichment coefficient is about 3×10^{3}.

Enrichment Process: the following solutions were prepared: a) 10 g of test tartaric acid was dissolved in 50 ml of distilled water; b) 10 g of the same material was dissolved in 41 ml of distilled water and the test elements added in amounts corresponding to the permissible norms for these elements as impurities, and the volume finally made up to 50 ml with distilled water.

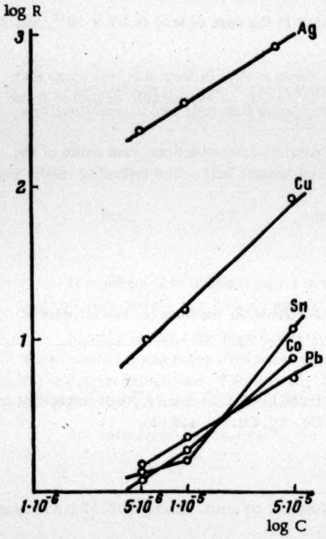

Fig. 3.

Chemically pure ammonia (25%) was then added to each solution until the pH was 5.5 (indicator paper).

Twenty mg of spectrographically pure carbon powder was added to each solution.

0.5 ml of 1% aqueous solution of sodium diethyldithiocarbamate is added at 30°* to each solution, the whole being carefully mixed by shaking, and then allowed to stand for 15 min. Hydrogen sulfide** is next passed through the solution for 5 min, and the precipitates filtered off through a 1.5 cm diameter ashless filter paper on a Buchner funnel; the precipitates are subsequently washed with an equal amount of water, and the pH adjusted to 5.5 with ammonia. The filter papers plus their precipitates are dried. The precipitates are then analyzed spectrographically. A "blank" is carried out (without tartaric acid) with the same amounts of reagents.

Determination is carried out on an ISP-28 spectrograph in a dc arc (220 v, 8 amps) with carbon electrodes. The lower electrode (anode) should have a cylindrical channel 4 mm deep and 4.2 mm in diameter. The upper electrode has a flat end face. A three-lens illumination system with a stepwise attenuator is used. All the precipitate (without the filter paper) is placed with 1 mg spectrographically pure NaCl [8] in the channel of the lower electrode. The spectra of the concentrates from solutions "a" and "b" and from the "blank" are photographed 2-3 times on one photographic plate. The exposure is 3 min at a slit width of 0.015 mm; photographic plates type 1.2 with a sensitivity of 8 GOST units are used.

The following lines are photometrically measured:

Co 3453.0; Ag 3280.7; Pb 2833.1
Cu 3247.0; Sn 2839.9.

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* Ammonium bitartrate precipitate cannot be permitted.

** Hydrogen sulfide must be passed through the solutions to ensure complete precipitation of tin.

By measuring the blackening of these lines and the adjacent background the values of $\Delta S = S_{\text{impurity}} - S_{\text{background}}$ are found. The values of $\log \frac{I_{\text{impurity}}}{I_{\text{background}}}$ are then determined for all these spectra. After conversion to intensities the content of the impurities in the test sample is calculated by extrapolation using the "method of additions."

TABLE 2

Sample no.	Analytical method	Impurity content, %				
		cobalt	silver	copper	tin	lead
1	Chemico-spectrographic	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$2\cdot10^{-6}$	$7\cdot10^{-6}$	$4\cdot10^{-6}$
		$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$1{,}2\cdot10^{-6}$	$6{,}6\cdot10^{-6}$	$6\cdot10^{-6}$
	Chemical	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<3\cdot10^{-6}$	—	—
2	Chemico-spectrographic	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$4\cdot10^{-6}$	$1{,}0\cdot10^{-5}$	$1{,}2\cdot10^{-5}$
	Chemical	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<5\cdot10^{-6}$	—	—

The sensitivity of copper and silver determination is about 1.0×10^{-6}%, while that for the remaining elements is 3.0×10^{-6}%. Only about 0.003% of lead can be detected directly in tartaric acid using an activated arc.

Thus the coefficient of the increases in sensitivity of a determination in the case of lead is $1.0 \times 10^{+3}$, while the theoretical enrichment coefficient is 5×10^2.

The relation between log R (log of relative intensity) and log C is shown in Fig. 3; from this it is clear that over the concentration range 5×10^{-6} - 5×10^{-5}% it is only in the case of tin that an appreciable deviation from linearity is observed.

In order to establish the reproducibility of the method developed, parallel determinations were made of the relative intensity of the spectral lines of the test elements in one sample of tartaric acid. The following results were obtained.

	Cobalt	Silver	Copper	Tin	Lead
Maximum deviation of the intensity (%) from the mean value	±9	±21	0	±38	±6

Table 2 contains the results obtained by chemico-spectrographic and chemical methods for two samples of tartaric acid.

SUMMARY

A chemico-spectrographic method is suggested for the determination of 1×10^{-6} - 1×10^{-5}% of impurities in sodium and potassium chlorides (Sn, Pb, Cd, and Bi) and in tartaric acid (Co, Ag, Cu, Sn, and Pb).

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THE DETERMINATION OF WATER

A. L. Gol'dinov, V. I. Lukhovitskii, and G. Ya. Mal'kova

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Among the numerous methods used for the determination of water content, methods based on the interaction of water with magnesium nitride and with calcium carbide and hydride have found wide application. The amount of water present is determined on the basis of the amount of ammonia, acetylene, and hydrogen respectively liberated. An essential feature in these cases is the relationship between the amounts of water present and the amounts of ammonia, acetylene, and hydrogen formed, the latter being dependent on the final reaction products. For example, during the reaction between water and magnesium nitride, $\frac{1}{3}$ or $\frac{2}{3}$ of a mole of ammonia will be liberated per mole of water, depending on whether the reaction follows equations (1) or (2).

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3, \tag{1}$$

$$Mg_3N_2+3H_2O=3MgO+2NH_3. \tag{2}$$

Similarly in the case of the reaction of water with calcium carbide and hydride, the relative amounts of water and acetylene or hydrogen will depend on the formation of calcium oxide or hydroxide as the result of the reaction:

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2, \tag{3}$$

$$CaC_2+H_2O=CaO+C_2H_2, \tag{4}$$

$$CaH_2+2H_2O=Ca(OH)_2+2H_2O, \tag{5}$$

$$CaH_2+H_2O=CaO+2H_2. \tag{6}$$

It is assumed in original papers and in textbooks [1-4] that the reactions between water and magnesium nitride, and calcium carbide and hydride are those given by equations (1), (3), and (5).

Bearing in mind the high reactivity of magnesium nitride, and calcium carbide and hydride, we assumed that these materials can react with the magnesium or calcium hydroxides formed according to equations (1), (3), and (5). Accordingly, interaction of water with Mg_3N_2, CaC_2, and CaH_2 with a quantitative yield of $Mg(OH)_2$ and $Ca(OH)_2$ according to equations (1), (3), and (5) in the presence of excess Mg_3N_2, CaC_2 and CaH_2 has a low probability.

We calculated the changes in the thermodynamic potentials for the reactions:

$$Mg_3N_2+3Mg(OH)_2=6MgO+2NH_3, \tag{7}$$

$$CaC_2+Ca(OH)_2=2CaO+C_2H_2, \tag{8}$$

$$CaH_2+Ca(OH)_2=2CaO+2H_2. \tag{9}$$

Table 1 contains the values of the thermodynamic potentials of all the compounds participating in reactions (7), (8), and (9).

We could not find any published values for the thermodynamic potential of magnesium nitride. We accordingly calculated this value from the known heat of formation of magnesium nitride (110.24 kcal [10]) and on the basis of the entropy of formations ΔS, calculated by Kireev's method [14] according to the formulas:

$$\Delta S_0=S-\Sigma n_{el}\,(S_{el})_i \tag{10}$$

$$\Delta S=\Delta S_0-[\Sigma n_{el}\cdot S_{el}-\Sigma n_{el}\,(S_{el})_i], \tag{11}$$

where: ΔS_0 is the entropy of formation of the compound from the elements found in the ideal state of a monoatomic gas; S is the entropy of the compound; n_{el} is the number of atoms of the given element in a molecule; S_{el} is the entropy of the element; and $(S_{el})_i$ is the entropy of the element in the state of an ideal monoatomic gas.

In order to calculate ΔS for magnesium nitride according to formula (11) we used the value of ΔS_0 for calcium nitride, a similar type of compound, calculated by means of formula (10).

TABLE 1. Thermodynamic Potential Values

Compound	ΔZ, 25°, kcal/mole	Literature cited	Compound	ΔZ, 25°, kcal/mole	Literature cited
CaC_2	— 16,2	[5]	CaO	—144,4	[6]
CaH_2	— 35,8	[6]	C_2H_2	+50,000	[8]
$Ca(OH)_2$	—214,33	[6]	NH_3	— 3,976	[9]
$Mg(OH)_2$	—199,27	[7]	Mg_3N_2	—95,5	—
MgO	—136,13	[7]			

The entropy values taken are given in Table 2.

$\Delta S_{0\,Ca_3N_2}$ = -159.21 electron units; $\Delta S_{Mg_3N_2}$ = -48,56 electron units, from which $\Delta Z_{Mg_3N_2}$ = -95.49 kcal/mole.

From the data given in Table 1 we find that

for reaction (7) $\Delta Z - 131.42$ kcal/mole; $K = 10^{96}$

for reaction (8) $\Delta Z - 8.27$ kcal/mole; $K = 1.1 \cdot 10^5$;

for reaction (9) $\Delta Z - 38.67$ kcal/mole; $K = 2.5 \cdot 10^{27}$

It follows from this that reactions (7), (8), and (9) are almost irreversible. Possible inaccuracies in the determination of the value of $\Delta S_{Mg_3N_2}$ should not essentially effect the value of ΔZ for reaction (7) because of the large value of the latter.

Thus during determination of water by the nitride method for example, if the interaction of water with magnesium nitride goes to completion, calculation of the amount of water should be made in accordance with equation (2), not by equation (1) as is generally accepted at present. The possibility is not excluded of course that the reaction ceases with formation of magnesium hydroxide, as a result, for example of the slow rate of reaction (7).

TABLE 2. Entropy Values

Compound	S and S_{el} (25°)	$(S_{el})_i$ (25°)	Literature cited
Ca_3N_2	25	—	[11]
Ca	9,95	36,993	[6]
Mg	7,77	35,504	[12]
N_2	45,767	—	[13]
N	—	36,6147	[13]

The position is the same for determination of water by means of calcium carbide and hydride.

It is of interest to note that during water determination with calcium hydride, higher results are obtained for the water content in those cases where the samples interact with calcium hydride for a long time [15]. The author of [15] does not explain this fact but it is readily explained by the possibility that reaction (9) occurs. We have carried out some experimental checks using magnesium nitride as an example.

Experimental. We chose determination of water in dichlorodifluoromethane (Freon 12) as the subject of our study. According to GOST 8501-57 this determination is carried out as follows.

Magnesium nitride is placed in a U-tube and is purged with nitrogen dried over phosphorus pentoxide. After the U-tube with Mg_3N_2 has been purged it is connected to a cylinder of the test gas. Freon is then passed for one hour at the rate of 7-8 liter/hr over the magnesium nitride.

An absorption apparatus containing 3 ml of 0.01 N HCl is then connected between the tube and the gas counter. Three liters of Freon is then passed through at a rate of 7-8 liters/hr.

The NH_3 in the absorption solution is then determined photometrically with Nessler reagent. The water content of the Freon is then calculated by means of equation (1).

A check on this method showed that the experimental results of determinations carried out at different times are not reproducible. It was established that even samll variations in the temperature of the room in which the experiments were carried out appreciably affect the results.

A series of determinations according to GOST 8501-57 were carried out, but during this series the tube containing magnesium nitride was thermostatted. Results for two samples of Freon 12 over the temperature range 0-25° are given in Table 3.

In addition, sample No. 1 was also analyzed at 120° and 600°. The temperature of 120° was chosen in accordance with recommendations accepted in [1]. The water content was calculated according to equation (1). We chose 600° because at this temperature magnesium hydroxide is certain to decompose into MgO and H_2O.

TABLE 3. Determination of Water in Freon at Different Temperatures

Temp, °C	H_2O found % wt.		Temp, °C	H_2O found % wt.	
	sample no.1	sample no. 2		sample no.1	sample no.2
0*	0,0019	—	20*	0,0034	0,0067
5*	—	0,0033	25*	0,0058	0,0089
10*	0,0038	0,0043	120*	0,0185	—
15*	—	0,0042	600**	0,0081	

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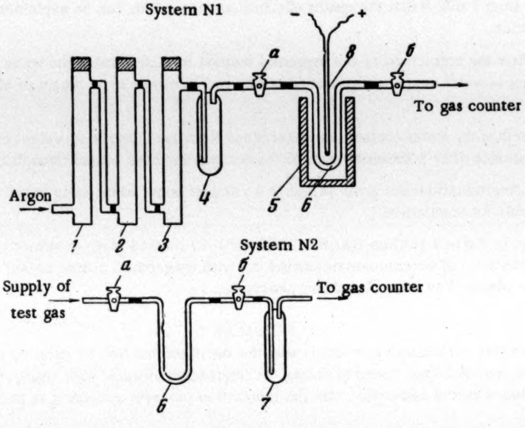
* The amount of water was calculated by means of equation (1).

** The amount of water was calculated by means of equation (2).

The experiments at 120° and 600° were carried out as follows (see diagram).



Setup for the determination of water content at 600°. 1) Drying column of $CaCl_2$; 2 and 3) drying columns of P_2O_5; 4) trap; 5) oven; 6) quartz tune with Mg_3N_2; a,b three-way taps; 7) absorber containing 0.01 N H_2SO_4; 8) thermocouple.

The nitride containing tube was purged at the temperatures indicated at the rate of 7-8 liters/hr with argon carefully dried over P_2O_5. Purging at 120° was carried out until the ammonia content of the argon after passing through the nitride tube had dropped to 5 μg/liter, and had dropped to zero at 600°.

An absorption apparatus containing 3 ml of 0.01 N H_2SO_4 was then connected between the nitride tube and the gas counter, and 3-5 liters of the test Freon and two liters of dried argon passed in succession through the nitride tube.

Purging of the nitride tube with argon is essential for removal of Freon. Otherwise, as experiment showed, very high results are obtained as a result of the interaction of Freon with magnesium at the high temperatures used with liberation of ammonia. After removal of Freon the nitride tube was placed in an oven heated to 120 or 600° respectively and purged with 5 liters of dried argon.

The amount of ammonia in the absorption solution was determined with Nessler reagent on a FEK-M photocolorimeter.

From a comparison of the experimental results obtained at 120 and 600° it follows that magnesium nitride reacts quantitatively with water even at 120° according to equation (2) and not according to equation (1) as Isakov et al. considered [1].

TABLE 4. Results for the Determination of Water in Nitrogen

Mg_3N_2		P_2O_5	Mg_3N_2		P_2O_5
t=600°	t=22–23°	H_2O, % wt.	t=600°	t=22–23°	H_2O, % wt.
H_2O, % wt.	H_2O, % wt.		H_2O, % wt.	H_2O, % wt.	
0,026	0,014	0,024	0,031		
0,028	0,011	0,024	0,032		
0,027	0,0103	0,028	0,0325		
0,032	0,011		0,0326		
0,0268	0,012				

It is also clear from Table 3 that determination of the water content by GOST 8501-57 is not feasible, since the results are sharply dependent on the temperature of the magnesium nitride.

It should also be noted that calculation of the water content according to equation (1) should give high results. Meanwhile it is clear from Table 3 that the results obtained are low. This can be explained by adsorption of ammonia by magnesium nitride.

In order to confirm the correctness of the suggested method for determining the water content of the gas, a series of determinations of water contents was carried out by two methods; 1) by means of Mg_3N_2 at 600°; 2) with phosphorus pentoxide.

In the second method the water content was determined from the increase in weight of an absorption tube containing phosphorus pentoxide after a known amount of the test gas had been passed through the pentoxide.

Results of these determinations are given in Table 4. Results obtained on using GOST 8501-57 at 22-23° are also included in the table for comparison.

The results given in Table 4 confirm that the GOST 8501-57 method gives incorrect results, and demonstrate the satisfactory reproducibility of determinations carried out with magnesium nitride at 600° and the agreement of these results with those obtained on using phosphorus pentoxide.

SUMMARY

It has been shown that the methods commonly used for the determination of water on the basis of the amounts of ammonia, acetylene, and hydrogen liberated during the interaction of water with Mg_3N_2, CaC_2, and CaH_2 respectively, and which are based on the assumption that the interaction proceeds according to the equations:

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3,$$
$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2,$$
$$CaH_2+2H_2O=Ca(OH)_2+2H_2,$$

are erroneous. The interaction of e.g. Mg_3N_2 with the same amount of water can give rise to different amounts of ammonia depending on the temperature. In particular the method of determining water in Freon 12 by means of GOST 8501-57 is incorrect.

A method of determining water with Mg_3N_2 is suggested which is based on carrying out the reaction at 600°; this ensures that ammonia is formed stoichiometrically according to the equation $Mg_3N_2 + 3H_2O = MgO + 2NH_3$.

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BRIEF COMMUNICATIONS

DETERMINATION OF SEXIVALENT CHROMIUM IN CATALYSTS FOR OLEFIN POLYMERIZATION

A. I. Perel'man and A. I. Antonova

Institute of Petroleum Chemical Synthesis, Academy of Sciences, USSR, Moscow

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Original article submitted May 13, 1960

A chromium catalyst prepared by impregnating alumino-silicate with chromium trioxide is used for the polymerization of olefins [1-3]. During its heat treatment, with the aim of dehydrating the alumino-silicate, the chromium trioxide undergoes a stepwise loss of oxygen with formation, apparently, of chromium and aluminum chromates [4,5].

The generally known iodometric method of determining sexivalent chromium only permits determination of water soluble chromium ions in the chromium catalyst, and not chromium in the form of chromium chromate and aluminum chromate because of the insolubility of these chromates in water.

During a study of the effect of chemical composition on the activity of a chromium catalyst the problem arose of developing a method which would permit determination of sexivalent chromium in water-insoluble chromates. The method which we would like to suggest for determination of sexivalent chromium is based on the capacity of CrO_3 (independent of what form it is in) to liberate oxygen on heating ($2CrO_3 \rightarrow Cr_2O_3 + 3O$) and on its subsequent entertainment. There are published references to the determination of oxygen in inorganic compounds, e.g., in zinc oxide [6] by its reduction with carbon:

$$ZnO + C = Zn + Co.$$

The carbon monoxide liberated is determined by different methods. Korshun [7] adopted the principle of this method for direct determination of oxygen in organic compounds. The method is based on decomposition of the organic compound and trapping the oxygen in the form of CO_2 which is obtained by oxidizing CO with iodine pentoxide. It was suggested subsequently that cupric oxide be used for oxidizing CO to CO_2 [8].

Essentially, as applied to chromium catalysts, the method consists in heating the products of thermal decomposition (at 900° for 3 hr) of chromium trioxide with platinum black in an inert gas current. The oxygen, formed as the result of the thermal decomposition of the catalyst, is quantitatively converted into CO. The latter is passed through cupric oxide at 380°, the monoxide is thereupon oxidized to CO_2; the CO_2 is determined from the increase in weight of askarite. The amount of CO_2 formed should not exceed 4-5 mg; accordingly the weight of catalyst taken (weighed on a microbalance) should be 20-30 mg. The apparatus used for determination of oxygen in the catalyst is shown in Fig. 1 in M. O. Korshun and N. E. Gel'man's book [9]. The nitrogen in which the determination is carried out must be purified very carefully.

The content of sexivalent chromium is calculated from the amount of oxygen formed and the carbon dioxide obtained on heating the catalyst.

The alumino-silicate used as carrier still contains 1.5-2% of water (as determined from the loss in weight of the alumino-silicate on calcining to 1200°) even after thermal treatment at 500°. This water decomposes during the determination with liberation of oxygen, which, at 1000° in the presence of platinum black, forms CO and then CO_2. Accordingly, the oxygen content of the alumino-silicate carrier must be determined.

The amount of sexivalent chromium is calculated by means of the formula

$$\%Cr^{VI} = \left(\frac{B'-x}{a'}\right) - \left(\frac{B-x}{a}\right) \cdot 36{,}36 \cdot \ 2{,}1666 = \left[\frac{(B'-x)}{a'} - \frac{(B-x)}{a}\right] \cdot 78{,}78,$$

where B' is the increase in weight of the askarite, mg (corresponding to the amount of CO_2 formed on heating the chromium catalyst); B is the increase in weight of the askarite, mg (the amount of CO_2 formed on heating the alumino-silicate); a' and a are respectively the weight (g) of the catalyst and alumino-silicate; 0.3636 is the conversion factor O/CO_2; 2.1666 is the conversion factor $2Cr/O_3$; and x is the increase in weight of the askarite in the blank.

TABLE 1. Determination of Cr^{VI} in Chromium Oxides by the Thermal Decomposition Method

Oxide*	Amount, %				Cr^{VI} found iodometrically, %
	active oxygen		Cr^{VI}		
	theoretical value	determined experimentally	theoretical value	determined experimentally	
CrO_3	24	24.2	52.00	52.43	52.2
$Cr_2(Cr_2O_7)_3$ dichromate	18.80	18.60	40.73	40.29	30.0
$Cr_2(CrO_4)_3$ monochromate	15.92	15.98	34.49	34.62	0
Chromium oxide Cr_2O_3	absent				

Note. Chromium oxides, and dichromate and monochromate, and chromium oxide were prepared from $Cr(OH)_3$. Their composition was checked by a differential thermal method, thermogravimetrically, and by x-ray analysis*.

TABLE 2. Determination of Cr^{VI} in a Chromium Catalyst (Heated beforehand at 500°)

Chromium content, %	Cr^{VI} found in the catalyst, %		By the method developed
	iodometrically	notes	
3-4	1.70	1.68	Mean values of two determinations.
5-6	3.55	2.77	
6-8	5.00	4.00	

The method of determining sexivalent chromium on the basis of the oxygen content was checked on a series of chromium oxides (Table 1).

The mean results of two determinations are given in the table.

As Table 1 shows, the iodometric method of determining Cr^{VI} gives low results for water-insoluble oxides.

The results in Table 2 show that the results obtained by the two methods of determining Cr^{VI} agree with each other, as long as the catalyst does not contain more than 4% of chromium.

The method developed makes it possible to follow those changes which the catalyst may be subjected to during reaction, by determining both the water soluble and water insoluble sexivalent chromium in it.

SUMMARY

A method has been developed for the determination of chromium (VI) in a chromium catalyst used for olefin polymerization; it is based on the capacity of CrO_3 to liberate oxygen on heating. The amount of Cr (VI) in the catalyst is calculated from the amount of oxygen evolved and the equivalent amount of carbon dioxide formed from it.

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A NEW PHOTOMETRIC METHOD FOR DETERMINATION OF VANADATES

L. P. Senetskaya and M. M. Teplyakov

D. I. Mendeleev Moscow Chemico-Technological Institute

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We have developed qualitative and quantitative methods for determination of vanadates which are based on the interaction of vanadates with α-naphthylamine in the presence of oxalate ions in a weakly acid medium, with subsequent extraction of the blue reaction product with n-butanol. Fe^{3+}, Ti^{4+}, Mo^{VI}, W^{VI} and other ions do not interfere. Popov [1] was the first to use α-naphthylamine in the presence of nitric acid (1:3) for detecting vanadates. This reaction has not been used for quantitative determination.

Vanadates are detected as follows: one drop of test solution and 4-5 drops of n-butanol are added to a mixture consisting of one drop of 0.1-0.5 N ammonium oxalate solution, one drop of 0.5-2 N sulfuric acid, and one drop of an acetic solution of α-naphthylamine (2 g/liter). A blue color which rapidly changes to violet in the n-butanol layer indicates the presence of vanadates in the test solution. The limit of identification is 4 μg of vanadate ion; the limiting dilution is 1:40,000.

The optical density of the extracts obtained is measured for quantitative determination. A standard series is prepared as follows in order to construct a calibration curve. Vanadate solution is measured out of a microburet into a measuring cylinder, the amount taken being such that the vanadate ion content is not less than 0.1 mg. One ml of α-naphthylamine solution (2 g/liter), five drops of 2 N sulfuric acid, and five drops of 0.5 N ammonium oxalate solution are then added. The solution obtained is diluted to 5 ml with water. After 5 min the colored compound is extracted four times with n-butanol. The extracts are transferred to a measuring cylinder which can be drained from the bottom, the water is allowed to drain off and the volume of the butanol layer made up to 10 ml.

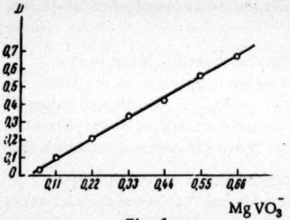

Fig. 1.

The optical density is measured 40-60 minutes after extraction, a FEK-M photocolorimeter fitted with a green filter being used. The extracts confirm to Beer's law (Fig. 1).

TABLE 1. Determination of Vanadium in Synthetic Mixtures

Mixture No.	Content of other ions, mg	VO_3^- taken, mg/10 ml	VO_3^- found, mg/10 ml	Error (relative), %	Mixture No.	Content of other ions, mg	VO_3^- taken, mg/10 ml	VO_3^- found, mg/10 ml	Error (relative), %
I	Fe^{3+} – 100	0.110	0.113	+2.73	III	MoO_4^{2-} –50	0.110	0.112	+1.8
		0.330	0.328	-0.61			0.330	0.330	0.00
		0.550	0.554	+0.73			0.550	0.547	-0.55
II	WO_4^{2-} –50	0.110	0.108	-1.8	IV	Ti^{4+} –50	0.110	0.115	+4.5
		0.330	0.326	-1.21			0.330	.0325	-1.5
		0.550	0.547	-0.55			0.550	0.555	+0.91

Vanadate ions were determined by this method in synthetic mixtures in the presence of Fe^{3+}, WO_4^{2-}, Ti^{4+} (Table 1), and also in various marks of steel (Table 2). An aliquot of test material was dissolved by the usual method [2]. $KMnO_4$ was used for oxidizing quadrivalent vanadium, excess $KMnO_4$ being removed with sodium nitrite. Excess nitrite was removed with urea. The solution obtained was quantitatively transferred to a standard flask.

TABLE 2. Determination of Vanadium in Steels

Mixture No.	V content, %	V content, %	Error (relative), %	Mixture No.	V content, %	V content, %	Error (relative), %
1	0.240	0.242	+0.83	2	0.30	0.295	-1.66
	0.240	0.239	-0.42		0.30	0.310	+0.34
	0,240	0.237	-1.22	3	1.39*	1.32	-5.02
2	0.30	0.300	±0.00		1.39*	1.38	-0.72
					1.39*	1.41	+1.44

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* The steel contains 17.68% W.

SUMMARY

A phtocolorimetric method has been developed for the determination of vanadates; it is based on the interaction of vanadate with β-naphthylamine in the presence of oxalate ions in a weakly acid medium.

Iron (III), titanium, molybdenum (VI), and tungsten (VI) ions do not interfere with vanadium determination.

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COMPLEX FORMING REACTIONS BETWEEN FERRIC IRON AND MANNITOL

A. V. Pavlinova and N. M. Cherkasova

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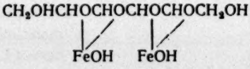
It is suggested in Nikitina's textbook [1] that iron can be complexed with mannitol during the titrimetric determination of aluminum with tartrates. No information is given on the composition and properties of the complex formed with mannitol. Consequently we decided it would be interesting to study this complex formation reaction.

The fact that complex formation does not occur is indicated by the intense yellow color of an iron salt solution after addition of mannitol, and by the fact that ferric hydroxide is not precipitated on adding alkali until the pH is 9. During this reaction it is essential to take a large excess of mannitol: for a 0.1 N solution of an iron salt a six-fold excess is taken, while for a 0.015 N solution a sixteen-fold excess is necessary. A considerable amount of alkali is used up in neutralizing the solution of mannitol and iron salt. In order to determine this amount and in order to choose an indicator for titration, three solutions were prepared, each containing 0.000473 g·mole of $FeCl_3$, and 0.00149, 0.00528, and 0.01056 g·mole of mannitol respectively. Titration curves were constructed for each solution (Fig. 1). 0.4736 N alkali was used as titrant. pH was measured on a LP-5 potentiometer using calomel and glass electrodes.

Fig. 1 shows that solutions containing ferric iron and mannitol titrate like strong acids. Excess mannitol does not affect either the nature of the curve or the amount of alkali used. During this titration three equivalents of acid correspond to 1 gram atom of iron (3 ml of 0.4736 N alkali was used up on 0.000473 g·atom of iron, i.e., 0.00142 g·eq).

A precipitate separates out in all cases at pH of about 5, but it dissolves on further addition of alkali until the pH is about 9. In appearance the precipitate is reminiscent of basic iron salts; it contains iron and carbon (CO_2 is liberated on calcining with cupric oxide). The compound of iron with mannitol separates out in the form of a yellowish-brown precipitate which is very fine and is difficult to filter. On drying in air the volume of the precipitate decreases considerably and it darkens; it is sparingly soluble in water but dissolves readily in alkali.

A precipitate which was separated in a large volume of alcohol was washed with 50% ethanol to remove excess mannitol was dried at 105° and then calcined in a muffle furnace. The residue left after calcination was dissolved in hydrochloric acid, and the iron determined gravimetrically. Carbon was determined on a separate aliquot by calcining with cupric oxide and absorbing the CO_2 with alkali. 22.11% Fe and 15.75% C were found; these values correspond to a ratio of Fe: mannitol of 2:6, i.e., one molecule of mannitol corresponds to 2 atoms of iron. This suggests that the following compound is formed:



$$\begin{array}{c} \mathrm{CH_2OHCHOCHOCHOCHOCH_2OH} \\ \mathrm{FeOH}\qquad\mathrm{FeOH} \end{array}$$

The precipitate does not loose all the water at 105°; an appreciable fraction of it is liberated at higher temperatures. The following results were obtained after introducing a correction water:

Found: 32.95% Fe; 23.36% C; 45.90% loss on calcining
Calculated: 34.57% Fe; 22.22% C; 50.61% loss on calcining

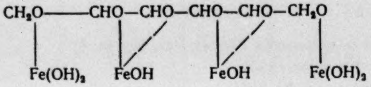
In order to determine the composition of the compound formed on increasing the pH, and to dissolve the precipitate, the latter was precipitated from an alkaline solution (pH about 9) by addition a three-fold amount of ethanol (96%). In order to check on the purity of the precipitated compound, it was reprecipitated with ethanol. The analytical results obtained before and after reprecipitation are given below:

Found before reprecipitation 43.16% Fe; 14.74% C; 41.36% loss on calcining

Found after reprecipitation 43.31% Fe; 14.66% C; 43.04% loss on calcining
Calculated 44.62% Fe; 14.34% C; 42.22% loss on calcining

It is clear that the composition of the compound does not change on reprecipitation; this indicated that the compound has an individual character.

From the results obtained we find: Fe:C = 4: 6.3,or 4:6. The compound has the formula:



Ferric hydroxide is not precipitated in a weakly acid medium (pH> 3)in the presence of mannitol; this indicates that complex formation starts even in an acid medium. In order to determine the composition of the compound formed under these conditions, mixtures of solutions of an iron salt and mannitol prepared by the isomolar series method were examined potentiometrically. The total concentration was the same for one series of experiments and equal to 0.0985 M. while it was 0.2735 M in another. The curves obtained are shown in Fig. 2. The composition of the mixture is plotted along the abscissa while the voltage in millivolts is plotted along the ordinate. A break corresponding to a ratio of Fe: mannitol = 2:3 is observed on both curves.

It has been established therefore that three complexes are formed between mannitol and iron: Fe_2Man_3 (where Man is mannitol) in an acid medium; $Fe_2(OH)_2Man$ in weakly acid and neutral media; and $Fe_4(OH)_6Man$ in alkali media. Complex formation proceeds stepwise, while the amount of hydroxyl groups whose hydrogen is substituted by iron increases with increasing pH.

In order to examine the interaction of the mannitol complex of iron with potassium tartrate we constructed titration curves of the tartrate complex of iron with alkali in the presence of and in the absence of mannitol. In one case 10 ml of potassium sodium tartrate 0.367 M was added to 10 ml of 0.2735 M $FeCl_3$ solution, while in the second case 10 ml of mannitol 0.565 M was added, and in the third 5 ml of potassium tartrate and 5 ml of mannitol were added.

The titration curves are shown in Fig. 3.

It is clear from Fig. 3 that the tartrate complex of iron (curve 1) titrates as a weaker acid than the complex with mannitol (curve 3). After addition of equal volumes of potassium sodium tartrate and mannitol, curve 2 is obtained, which lies between curves 1 and 3 and is more similar in character to the curve for the tartrate complex of iron. It can be deduced from this that some of the iron atoms change over from mannitol to tartrate.

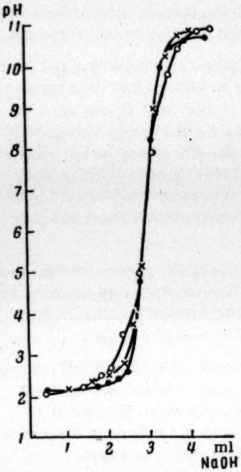


Fig. 1.

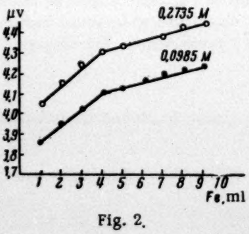


Fig. 2.

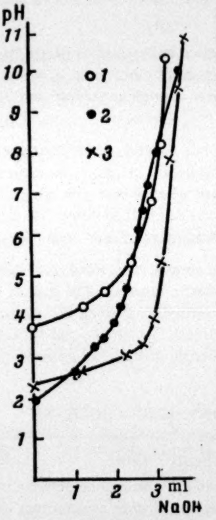


Fig. 3.

The results obtained helps one to explain the processes which occur during titration of aluminum by E. I. Nikitina's method.

According to this method aluminum is determined from the difference between the two volumes of alkali used in titrating a solution containing mannitol and potassium sodium tartrate, and the same volume of solution containing mannitol and sodium oxalate. In the first instance, the free acid, acid liberated during the interaction of iron with mannitol, and acid liberated during the interaction of aluminum with potassium sodium tartrate are titrated. In the second case the free acid and the acid from the reaction of iron with mannitol are titrated, since oxalate complexes aluminum as a neutral complex. E. I. Nikitina is of the opinion that in the second titration only the free acid is titrated. In fact, as our experiments have shown, iron liberates an acid with mannitol which is also titrated. But, since equal volume of solutions are taken for both titrations, while mannitol is added to each, this does not reflect on the difference in the volumes. Accordingly, mannitol does not affect determination of aluminum. In a solution containing potassium sodium tartrate, the mannitol complex partially breaks down and changes into a tartrate complex. But this does not affect the amount of acid liberated, since three equilvalents of acid are also liberated during formation of the tartrate complex [2].

SUMMARY

It has been established that iron forms three complexes with mannitol: Fe_2Man_3 in an acid medium, $Fe_2(OH)_2Man$ in weakly acid and neutral media, and $Fe_4(OH)_6Man$ in an alkaline medium (where Man equals mannitol).

It has been shown that iron can be titrated with alkali in the presence of excess mannitol using phenolphthalein as indicator, the solution being clear at the titration end point. The color of the indicator is readily observable; three equivalents of acid are titrated per iron atom.

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DETERMINATION OF RHENIUM IN COAL

V. V. Kuznetsova

M. V. Lomonosov Moscow State University

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Goldsmith and Peters [1], Ratynskii [2], Headlee and Hunter [3], Fuchs [4] and others have shown that coal ash, particularly brown coal ash, often contains appreciable amounts of vanadium, molybdenum, uranium, germanium, and nickel. During endogenic processes rhenium, a scattered element with a Clark number $1 \times 10^{-7}\%$, always accompanies molybdenum. Normal methods cannot be directly used for determination of rhenium in coal containing appreciable amounts of molybdenum. The basic difficulties involved in this case are connected with the very high volatility of rhenium oxides (Re_2O_7 volatilizes at 157°) [5], which leads to loss of rhenium. Experiment has shown that on ashing coal, up to 50% of rhenium is lost (Table 1). Aliquots of coal contained in porcelain crucibles were placed in a cold muffle furnace and the temperature taken up to 500-800°. Rhenium was determined in the ash by the thiocyanate photometric method [6].

On the basis that the stability of perrhenates is considerably higher than the stability of rhenium sulfides and oxides [5], we tried to combine ashing with sintering during the usual method of determining rhenium in sulfides and rocks [6].

To aliquots of coal (10 g) free from rhenium was added 20 g of CaO and 50, 20, 20, and 5 μg of rhenium. After sintering 600°, 48, 22, 18.5 and 5 μg of rhenium were found.

It is clear that in the presence of calcium oxide the decomposition temperature can be raised to 600-650° without any danger of loosing rhenium. At this temperature, and on adding potassium permanganate as oxidizing agent, the organic matter in the coal is oxidized while the rhenium and molybdenum form stable calcium perrhenate and molybdate. In order to ensure oxidation of organic residue, bromine water was added during the leaching process. Rhenium was determined photometrically in the form of its thiocyanate complex after removal of molybdenum with potassium butylxanthogenate in chloroform. At this stage, however, we came up against a new difficulty. Frequently, during analysis of natural coal, instead of the characteristic yellow colors of the thiocyanate complex of rhenium, we obtained yellow-green colors which could not be compared with the color of standard solutions. Such colors may be the results of high concentrations of vanadium, tungsten, niobium, chromium, and nickel [7-9]. Addition of citric or tartaric acid which complex tungsten into a colorless tartrate or citrate did not destroy the interfering color.

TABLE. 1. Loss of Rhenium during Ashing of Coal (Rhenium was added together with MoS_2)

Aliquot of coal free from rhenium, g	Re added, μg	Re found in the ash, μg	Loss of Re, %	Ashing temperature
5.1	10	6.4	36	500
5.4	10	5.6	44	800
10.0	50	28.3	43.4	500
10.2	50	24.5	51	800

Spectrographic analysis indicated that in addition to tungsten, the test coal samples contained appreciable amounts of vanadium (up to 0.11%), while the content of the remaining elements listed above did not exceed a few thousandths of a percent. The problem therefore reduced to making the green color of the vanadium thiocyanate compound. It is known [7] that vanadium, together with titanium, chromium, etc. forms a colorless complex with fluoride ions. Accordingly, in order to remove the green color caused by the vanadium, sodium fluoride solution was added (Table 2).

Analytical Procedure. An aliquot of about 20 g of coal is carefully mixed in a porcelain basin with 40 g calcium oxide and 1 g of potassium permanganate. A further 5 g of calcium oxide is strewn over the mixture. The crucible and its contents are placed in a cold muffle furnace, preferably with an air draught, and the temperature gradually taken up to 600°. The sample is sintered at this temperature for 6-8 hr. The sinter is leached by heating for about 2 hr on a water bath with water to which a few ml of bromine water has been added. The solution is filtered through a porous filter and the precipitate on the filter washed several times with hot water. The filtrate is evaporated into a 100 ml separating funnel. The volume of filtrate plus wash liquor should be about 30 ml.

TABLE 2. Effect of Sodium Fluoride on the Results of Determining Rhenium in the Presence of Vanadium

Introduced		5% NaF solution added, ml	Re found, μg	Note
V	Re, μg			
100 μg		5		Weak yellow-green color disappears after addition of NaF
1000 μg	50	10	51	
1000 μg	50	10	48	
10 mg	–	10 μg	–	Yellow-green color disappears 10-15 min after addition of NaF
10 mg	50	10	51.5	
30 mg	50	10	49	
30 mg	50	10	49.5	
20 mg	5	10	5.2	
20 mg	5	10	5.3	

Three ml of freshly prepared 10% solution of potassium butylxanthogenate and 10 ml of concentrated hydroacid are added to the solution in the separating funnel. The raspberry molybdenum-xanthogenate complex is extracted with chloroform (5 extracts with 10 ml portions of chloroform).

The molybdenum free solution is transferred into a 50 ml colorimeter cylinder and 10 ml of 5% sodium fluoride solution added. After several minutes, 3 ml of ammonium thiocyanate (20% solution), 2 ml of stannous chloride (35% solution in HCl), and 5 ml of isoamyl alcohol saturated with a mixture of the reagents used, are added in succession. The yellow color formed when rhenium is present is compared visually or on a colorimeter with the color of standard solutions prepared at 0.2 μg intervals over the concentration range up to 10 μg rhenium in 5 ml of isoamyl alcohol, and at 1 μg intervals over the rhenium concentration range 10 to 50 μg Re in 10 ml of isoamyl alcohol.

The accuracy of the method is ≠15%.

SUMMARY

A photometric method is suggested for the determination of small amounts of rhenium in coal, the rhenium is determined as its thiocyanate complex. Interference from vanadium is suppressed by addition of NaF. Coal samples are ashed by sintering with CaO and $KMnO_4$.

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A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN PHOSPHOSILICOORGANIC COMPOUNDS

K. A. Andrianov, L. M. Khananashvili, and
T. V. Vasil'eva

M. V. Lomonosov Moscow Institute of Fine Chemical Technology

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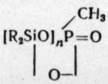
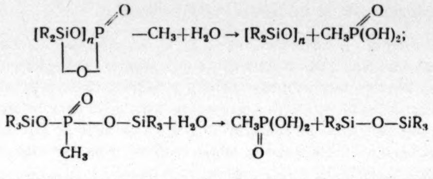
At present phosphorus is determined in phosphosilicoorganic compounds by combustion of the latter followed by separation of silicon from phosphorus. This method involves the long operation of precipitating PO_4^{3-} ions with ammonium molybdate and a titrimetric finish. In some cases, particularly during analysis of phosphosilicoorganic compounds, in which the phosphorus is connected to silicon via oxygen, simpler methods can be used. We should like to suggest that in order to determine phosphorus in phosphosilicoorganic compounds  $[R_2SiO]_nP(CH_3){=}O$ use be made of the capacity of such compounds to be completely hydrolyzed by water with formation of alkylphosphinic acid:



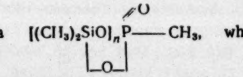
$$[R_2SiO]_nP(=O)-CH_3 + H_2O \rightarrow [R_2SiO]_n + CH_3P(=O)(OH)_2;$$

$$R_3SiO-P(=O)(CH_3)-O-SiR_3 + H_2O \rightarrow CH_3P(OH)_2(=O) + R_3Si-O-SiR_3$$

The method of determining phosphorus is very simple. 0.2-0.3 g of test material is dissolved in water and left to stand for 4-5 hr for the hydrolysis to go to completion. By heating to 80° the time necessary for complete hydrolysis can be reduced to 30-40 min. The alkylphosphinic acid liberated is titrated with 0.1 N alkali solution in the presence of thymolphthalein (pH 9.4-10.6). Results for the determination of synthetic mixtures of tetraethoxysilane and methylphosphinic acid are given in Table 1.

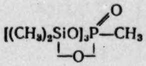
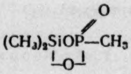
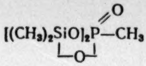
TABLE 1.

Taken, moles		Amt. of phosphorus, %(wt)		Difference
$CH_3PO(OH)_2$	$(C_2H_5O)_4Si$	calculated	found	
0,0067	0,018	4,76	4,98	+0,22
0,0025	0,0027	9,62	9,62	—0,00
0.0098	0,0071	12,63	12,59	—0,04
0,0098	0,0048	15,1	14,96	—0,14
0,0332	0,00825	20,9	20,73	—0,17

Compounds of the general formula  $[(CH_3)_2SiO]_nP(=O)-CH_3$, where n varied from 1 to 3 were analyzed by this method. Results which were in good agreement with the expected values were obtained in all cases (Table 2).

The agreement between parallel determinations is 0.2-0.3%

TABLE 2.

Compound	P, %		Difference	Compound	P, %		Difference
	found	calc.			found	calc.	
 $\underbrace{[(CH_3)_2SiO]_3\overset{O}{\overset{\|}{P}}}_{O}-CH_3$	10,28	10,25	—0,03	 $\underbrace{(CH_3)_2SiO\overset{O}{\overset{\|}{P}}}_{O}-CH_3$	20,34	20,18	0,16
 $\underbrace{[(CH_3)_2SiO]_2\overset{O}{\overset{\|}{P}}}_{O}-CH_3$	13,64	13,29	—0,25				

SUMMARY

For determination of phosphorus in phosphosilicoorganic compounds in which phosphorus is connected to silicon via oxygen, it is recommended that use be made of the capacity of such compounds to hydrolyze with water to form alkylphosphinic acid.

AMPEROMETRIC TITRATION OF ACETYLENE IN N-METHYLPYRROLIDONE AND IN DIMETHYLFORMAMIDE WITH SILVER NITRATE SOLUTION

Ya. I. Turn'yan and V. F. Romanov

State Scientific-Research and Design Institute of the Nitrogen Industry
and Products of Organic Synthesis, Lisichansk Branch, Severodonetsk

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Of considerable practical and theoretical interest is an examination of the possibility of using the well-known precipitation reaction of silver acetylide for the purpose of developing a direct method for the amperometric titration of C_2H_2 dissolved in N-methylpyrrolidone or in dimethylformamide.

Acetylene prepared from calcium carbide was purified with chromic mixture, cadmium acetate, and distilled water; it was then dried with silica gel and finally absorbed with N-methylpyrrolidone ($n^{25} = 1.4671$ and $d_4^{25} = 1.0321$) or diemethylformamide ($n^{25} = 1.4279$ and $d_4^{25} = 0.9470$).

The concentration of the stock solutions (about 1 M C_2H_2) was determined by weighing the solvent [1] before and after saturation with acetylene, the necessary precautions being taken to preclude loss of C_2H_2.

For polarographic determination on a dropping mercury electrode it is best to use ammoniacal solutions of $AgNO_3$ (2-10% NH_3 + 0.1 M KNO_3) in which there is linear relation between the diffusion current and the silver concentration (in aqueous solution $K = 6.3$ μa/mM/liter, while in aqueous methanol solution containing 50% (by volume) of CH_3OH, $K = 5.5$ μa/mM/liter).

The diffusion current starts at zero potential (relative to a 0.1 N calomel electrode).

All titrations were carried out on the Czech LP 55 polarograph at a potential of -0.35 to -0.40 v.

The acetylene solution was always placed in a sealed buret. Back titration of C_2H_2 with $AgNO_3$ is impossible because the C_2H_2 is expelled from the solution during removal of dissolved oxygen. Oxygen was removed by passing nitrogen through the solution for 10 min; nitrogen was passed for 1-2 min after addition of each portion of titrant.

The amperometric curves were always corrected for dilution, since the C_2H_2 concentration was only 2-20 times greater than the $AgNO_3$ concentration (Table 1).

The capillary characterisitics were as follows $mg^{2/3}\, t^{1/6} = 2.45$ $mg^{2/3}\, sec^{-1/2}$ at $E = 0.4$ v. The cell was thermostatted at 25 ± 0.3°.

Aqueous methanol solutions (50% by volume of CH_3OH) were used for obtaining reproducible results in dimethylformamide. Under such conditions the solubility of the precipitate even increased slightly; nevertheless, the reproducibility of the results improved significantly, presumably as the result of an increase in the rate at which the acetylene is precipitated.

Characteristic amperometric curves (diagram) were obtained in all cases, the shape of these curves being influenced by the solubility of the precipitate at C_2H_2 concentrations less than 0.01 M. The reasonably large area over which the curves are linear makes it possible to determine C_2H_2 in N-methylpyrrolidone up to concentrations of 1×10^{-3} M, and in dimethylformamide up to 5×10^{-3} M (Table 1) with satisfactory accuracy.

It follows from the amperometric titration results that the following reaction occurs in ammoniacal solution:

$$C_2H_2 + Ag(NH_3)_2^+ + OH^- \rightarrow \underset{\downarrow}{\underline{C_2HAg}} + 2NH_3 + H_2O, \tag{1}$$

i.e., one mole of C_2H_2 reacts with one mole of silver.

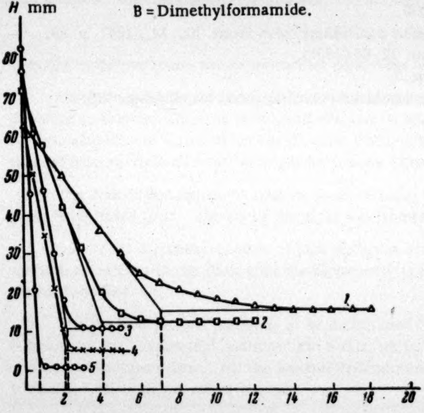
This relation was also confirmed by dissolving the precipitate in HNO_3 and determining the silver in solution.

Published information on the composition of silver acetylide is contradictory (C_2HAg, C_2Ag_2, $C_2Ag_2\cdot AgNO_3$) [2]. Presumably the pH of the solution affects the composition of the precipitate. The most likely composition of the precipitate which separates out of acid solutions is $C_2Ag_2\cdot AgNO_3$, while from a weakly acid (pH 4-5) buffered solution C_2Ag_2 separates out [1]. At higher pH values, as in our case, formation of C_2HAg would be expected.

TABLE 1.

C_{AgNO_3}, M	Solvent	C_2H_2 taken, M	C_2H_2 found, M	Error (relative) %
$5\cdot10^{-4}$	A	$1,02\cdot10^{-3}$	$1,07\cdot10^{-3}$	5,0
$5\cdot10^{-4}$	A	$1,50\cdot10^{-3}$	$1,56\cdot10^{-3}$	4,0
$5\cdot10^{-4}$	A	$2,01\cdot10^{-3}$	$1,97\cdot10^{-3}$	2,0
$5\cdot10^{-4}$	A	$3,17\cdot10^{-3}$	$3,02\cdot10^{-3}$	5,0
$1\cdot10^{-3}$	A	$5,02\cdot10^{-3}$	$4,96\cdot10^{-3}$	1,0
	B	$4,80\cdot10^{-3}$	$5,00\cdot10^{-3}$	4,0
$1\cdot10^{-3}$	A	$1,00\cdot10^{-2}$	$0,98\cdot10^{-2}$	2,0
	B	$0,96\cdot10^{-2}$	$0,95\cdot10^{-2}$	1,0
$2,0\cdot10^{-3}$	A	$2,05\cdot10^{-2}$	$2,00\cdot10^{-2}$	2,5
$2,5\cdot10^{-3}$	B	$2,40\cdot10^{-2}$	$2,38\cdot10^{-2}$	1,0
$5,0\cdot10^{-3}$	A	$4,65\cdot10^{-2}$	$4,75\cdot10^{-2}$	2,0
	B	$4,80\cdot10^{-2}$	$4,87\cdot10^{-2}$	1,5
$5,0\cdot10^{-3}$	A	$8,20\ 10^{-2}$	$8,30\cdot10^{-2}$	1,2
	B	$9,60\cdot10^{-2}$	$9,78\cdot10^{-2}$	1,9
$5,0\cdot10^{-3}$	A	0,165	0,167	1,2
$1\cdot10^{-2}$	B	$9,60\cdot10^{-2}$	$9,78\cdot10^{-2}$	1,2
$1\cdot10^{-2}$	A	0,33	0,34	1,2

A = N-methylpyrrolidone.
B = Dimethylformamide.



Amperometric titration curves of C_2H_2 in N-methylpyrrolidone. 1 - $C_{C_2H_2} = 1\cdot10^{-3}$ M, $C_{AgNO_3} = 5\cdot10^{-4}$ M; 2 - $C_{C_2H_2} = 5\cdot10^{-3}$ M, $C_{AgNO_3} = 1\cdot10^{-3}$ M; 3 - $C_{C_2H_2} = 1\cdot10^{-2}$M, $C_{AgNO_3} = 1\cdot10^{-3}$M; 4 - $C_{C_2H_2} = 2\cdot10^{-2}$M, $C_{AgNO_3} = 2\cdot10^{-3}$M; 5 - $C_{C_2H_2}$ = 0.165M, $C_{AgNO_3} = 5\cdot10^{-3}$M

The solubility of acetylides decreases with increasing pH [3]. Ammonia, should, on the one hand, depress the solubility by increasing the pH, while on the other hand, it should increase the solubility as a result of complex formation with silver. As is to be expected (equation 1), changes in NH_3 concentration over the range 2-10% do not appreciably affect the character of the amperometric curves.

Using equation 1 and the instability constant $K_C = 2.75 \times 10^{-8}$ for $Ag(NH_3)_2^+$ [4], we calculated the "product of hydrolytic solubility" constant suggested by Babko and Grebel'skaya as a characteristic of the solubility of acetylides:

$$L_h = [Ag^+]\,[C_2H_2]\,[OH^-]. \quad (2)$$

For this purpose we initially found the value (all calculations were made for aqueous solutions):

$$L = [Ag\,(NH_3)_2^+]\,[C_2H_2] = \left(\frac{i_{equiv}}{K}\right)^2, \quad (3)$$

which for $[NH_3]$ = const and $[OH^-]$ = const is constant (Table 2) and characterize the limit of sensitivity of amperometric titration ($i_{equiv.}$ is the current strength at the equivalence point, and K is the diffusion current constant).

The value $L = 3.8 \times 10^{-8}$ (for $[NH_3] = 6.1$ and $[OH^-] = 1.0 \times 10^{-2}$M) shows [5] that the sensitivity of the technique should not be less than $10^{-3} - 10^{-2}$ M C_2H_2, this was actually observed experimentally.

TABLE 2.

C_{AgNO_3}, M	$C_{C_2H_2}$, M	i_{equiv}, μa	$L_h \cdot 10^8$
$5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	0,705	(1,3)
$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	1,27	4,1
$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	1,16	3,4
$2 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	1,24	3,9
$5 \cdot 10^{-3}$	0,165	1,25	3,9
		Mean	3,8

The value $L_h = 10^{-19}$. It was found in [3] that

$$L_h = [Ag^+]^2 [C_2H_2] [OH^-]^2 \cong 10^{-37}, \tag{4}$$

since it was assumed [3] that C_2Ag_2 is precipitated from ammoniacal solution. If the results on the solubility are used [3] and it is assumed, as we have established, that the composition of the precipitate is C_2HAg, the value obtained for L_h is about 10^{-20}. Bearing in mind that the solubility was studied [3] in very acid solutions, while our results were obtained in strongly ammoniacal solutions (the difference in $[OH^-]$ is more than ten times greater). the value of $L_h = 10^{-19} - 10^{-20}$ can be regarded as a fully reliable value for the precipitate of C_2HAg.

SUMMARY

A precipitation reaction of silver acetylide in which the diffusion current of silver ammonite ions is recorded, has been used for the amperometric titration of acetylene solutions (in a buret). The sensitivity of the reaction is 1×10^{-3}M of acetylene. The experimental accuracy is 1-2%(relative) for acetylene concentrations in excess of 5×10^{-3}M.

It has been established that the composition of the silver acetylide precipitated from ammoniacal solution corresponds to the formula $AgHC_2$; the hydrolytic solubility product of this precipitate has been found to be $L_h = 10^{-19} - 10^{-20}$.

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DETERMINATION OF PHOSGENE IN THE PRESENCE OF CHLORINE AND HYDROGEN CHLORIDE

A. P. Terent'ev, M. M. Buzlanova, and
S. I. Obtemperanskaya

M. V. Lomonosov Moscow State University

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We encountered considerable difficulties during determination of phosgene in the presence of chlorine and hydrogen chloride. A number of methods have been described; an iodometric method [1], and an aniline [2] method based on absorption of phosgene with an alcoholic solution of alkali, or with an ammoniacal solution of silver nitrate [3], with subsequent determination of halide gravimetrically or titrimetrically. All these methods only permit determination of phosgene in the absence of chlorine, hydrogen chloride, and other impurities. Antimony metal, antimony sulfide, mercury, and mercuric sulfide have been suggested for absorbing chlorine, while zinc dust has been suggested for absorbing hydrogen chloride. This complicates an analysis considerably.

We should like to suggest a new method for determining phosgene, which is based on the interaction of phosgene with hexamethyleneimine [4], with subsequent titration of excess of the latter after steam distilling it from an alkaline solution. Bis-hexamethyleneurea which is formed according to the equation:

$$4(CH_2)_6NH + COCl_2 \rightarrow (CH_2)_6N{-}CO{-}N(CH_2)_6 + 2(CH_2)_6NH \cdot HCl,$$

does not hydrolyze under the experimental conditions used.

Phosgene was prepared from carbon tetrachloride and oleum, it was purified by freezing it twice and was finally dissolved in toluene. Dioxane or toluene was used as solvent for hexamethyleneimine; toluene is less suitable because of its insolubility in water which complicates distillation and titration. Poor results were obtained with aqueous solutions of hexamethyleneimine, as might have been expected, because of the hydrolysis of phosgene with water.

The distillation apparatus consists of an ordinary Wurtz flask with an outlet tube bent through a right angle, a pipet being fused to it. The tip of the pipet was immersed in a measured volume of 0.1 N acid.

Results for the determination of pure phosgene are given in Table 1. As a control, the chloride content of the solution remaining in the flask after the hexamethyleneimine had been steam distilled off was determined by the Volhard method.

The method permits phosgene to be determined in the presence of chlorine and hydrogen chloride. The latter is bound by the hexamethyleneimine into a salt, while the chlorine forms a chloramine which can be destroyed by addition of sodium sulfite. All the hexamethyleneimine which has not been used up in forming the urea derivative is distilled off from the alkali solution.

An aliquot of phosgene in toluene, taken in an ampoule, was dissolved in dioxane in a standard flask. Phosgene was determined in one aliquot as described below. A solution of chlorine in carbon tetrachloride was added to another aliquot and the phosgene determined again. The amount of phosgene found in the pure sample and in the presence of chlorine coincides (Table 2).

Experimental Method. Pure Phosgene and Phosgene in the Presence of Hydrogen Chloride. An aliquot of a solution of phosgene in toluene (0.05-0.1 g), taken in an ampoule, is introduced into a flask with a ground stopper and 5 ml of a solution of hexamethyleneimine[*] in toluene or dioxane[**] (5 g of hexamethyleneimine in 100 ml solution), added from a pipet. The flask is stoppered and vigorously shaken; as a result the ampoule containing the phosgene is broken and the flask is allowed to stand for several minutes for the mist to settle. The contents of the flask are transferred to the distillation apparatus, it is rinsed with 30 ml of water, and 5 ml of 40% alkali solution added. Distillation is then carried out into 50 ml of 0.1 N acid. Excess acid is determined by titration with 0.1 N alkali using a mixed indicator of methyl red – methylene blue (40 ml of a 0.1% alcoholic solution of methyl red is mixed with 10 ml of a 0.1% alcoholic solution of methylene blue and 50 ml of alcohol and 100 ml of water added). The end point is established by a sharp change from rose to green. A blank is carried out in the same way (using the same amounts of reagents and carrying out the distillation) except that an aliquot of phosgene is not taken.

---

[*] The hexamethyleneimine is dried with solid potassium hydroxide and distilled, b.p. 138°.

[**] Dioxane is purified by distillation over sodium.

TABLE 1.

Wt. of $COCl_2$, taken, g	v***	$COCl_2$ found, %	
		on the basis of chlorine	on the basis of hexamethyleneimine
0,1011*	3,97	19,44	19,39
0,1047*	4,09	19,18	19,91
0,0403*	1,62	19,85	19,90
0,0734*	2,95	19,91	19,89
0,1280**	4,90	19,01	19,26
0,0633**	2,35	18,41	18,45
0,0992**	3,82	19,06	18,66

---

* Hexamethyleneimine in dioxane solution.

** Hexamethyleneimine in toluene solution.

TABLE 2.
(0.04836 g phosgene in toluene taken)

$COCl_2$, pure, %	$COCl_2$ in the presence of chlorine, %
15.97	16.32
15.77	16.21
16.21	15.97
16.20	15.77
Mean 16.04%	16.07%

The formula used for calculation is:

$$\%\,COCl_2\ \frac{(v_1-v_2)\cdot N\cdot M\cdot 100}{a\cdot 2\cdot 1000},$$

where v_1 is the amount in ml of alkali used for titrating the aliquot of phosgene; v_2 is the amount in ml of alkali used for titrating the blank; N is the normality of the alkali; M is the molecular weight of phosgene; a is the weight of the aliquot (in g).

Phosgene in the Presence of Chlorine. When the phosgene contains chlorine as an impurity, 5 ml of 0.5 N sodium sulfite solution (120 g of the heptahydrate in one liter of water) is added to the solution when the reaction between hexamethyleneimine and phosgene is complete; the determination is then finished as described above.

SUMMARY

A new method has been developed for the determination of phosgene which is based on the reaction of the latter with hexamethyleneimine, with subsequent determination of excess of the imine. The method permits determination of phosgene in the presence of chloride and hydrogen chloride.

LITERATURE CITED

1. M. P. Matuszak, Ind. Eng. Chem., Anal. Ed. 6, 457 (1934).
2. W. P. Jant, J. C. Olsen, and H. Storch, Ind. Eng. Chem., Anal. Ed. 8, 20 (1936).
3. J. C. Olsen and G. E. Ferguson, Ind. Eng. Chem., Anal. Ed. 3, 189 (1931).
4. S. I. Burmistrov and V. V. Egorova, Ukr. khim. zhurnal 24, 222 (1956).

CRITICISM AND BIBLIOGRAPHY

A. I. BUSEV. THE USE OF DIVALENT CHROMIUM COMPOUNDS IN ANALYTICAL CHEMISTRY

Moscow. Viniti AN SSSR, 1960, 164 pp. Bibl. 180 refs.
Reviewed by P. P. Shat'ko
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 745-746, November-December, 1961

Divalent chromium ions have a number of advantages as a reducing agent over other reducing agents (vanadyl sulfate, trivalent titanium salts, potassium stannite, sodium hydrosulfite, hypophosphorous acid etc.). The most important advantage of divalent chromium is its strong reducing capacity. The ease of preparation and storage of stable solutions of divalent chromium salts ensures the further introduction of chromometry into practical work as the author correctly points out. A. I. Busev's monograph is of undoubtedly great interest for a wide circle of analytical chemists as the first complete summary of accumulated experience in the application of divalent chromium compounds in analytical chemistry.

The first section of the book is devoted to general questions of the application of divalent chromium compounds in analytical chemistry. Methods of preparing, standardizing, and storing standard solutions of divalent chromium salts are described in detail.

The second section is devoted to the reduction reactions of elements with divalent chromium compounds and the use of such reactions in analytical chemistry. The heading of the second section does not correspond in all respects to its contents, since the author in this section gives a detailed review of methods for the quantitative determination and separation of the ions of different elements which are reduced by divalent chromium ions. Reduction of the following elements is considered: of group I elements Cu^{2+}, Ag^{+}, Au^{III} (pp. 28-39); of group II, Hg^{2+}, Cd^{2+} (pp. 39-41); of group III, Ce^{IV} (pp. 41-42); of group IV, Sn^{IV}, Ti^{IV} and carbon compounds (pp. 42-60); of group V, N^{V}, As^{V}, Sb^{V}, Bi^{III}, V^{V} (pp. 60-78); of group IV, O_2, S^{VI}, Se^{IV}, Te^{IV}, Cr^{VI}, Mo^{VI}, W^{VI}, U^{VI} (pp. 78-117); of group VI, Br_2, I_2^-, I^{V}, Br^{V}, Mn^{VII} (pp. 117-121); and of group VII, Fe^{3+}, Co^{III}, Ru^{III}, Os^{IV}, Rh^{III}, Jr^{IV}, Pe^{IV} (pp. 121-155). The methods indicated for the determination of each element in pure solutions, in mixtures, and in various samples are of practical importance (ores, special steels, etc.). The review of the reduction of organic compounds is of considerable importance, and this should be reflected in the heading.

A factor which complicates reading of the monograph is the absence of the names of the authors during a description of most of the methods of determination, only the ordinal number being given in the literature reference, and this sometimes leads to errors; thus on p. 72 (13 lines from the bottom) [122] is written whereas it should obviously be [123]. There are other small errors. On p. 10 (one line from the top) the author states that the "reducing properties of divalent chromium increase with decreasing acid concentration." We cannot agree with such an unconditional generalization, since it is known that the reducing properties of Cr^{2+} with respect to arsenates increase, rather than decrease, with increasing acid concentration. In dealing with the reduction of dichromate to a trivalent chromium salt by means of ethanol, concentrated hydrochloric acid, or hydrogen peroxide (p. 12), the author does not point out that such a reduction can be effected by means of ethanol and concentrated sulfuric acid.

Unfortunately, the methods of preparing solutions of divalent chromium salts are not given in chronological order. Thus the work of Stone and Bison (1936) is mentioned before that of Thornton and Sadex (132). Stone and Bison modified Thornton and Sadex's method. The author does not refer to Popov's method of preparing divalent chromium salts (Zavodsk. laboratoriya 12, 972 (1946)). We do not think it is a good idea to standardize the Cr^{2+} solution against ferric iron (p. 20) on the grounds that it necessitates a parallel titration of two solutions. The Cr^{2+} solution is best standardized against cupric sulfate, whose titer is established electrolytically. The method of microtitration in ultraviolet light should not be described on p. 28, since it does not belong to this chapter.

On p. 28 the author notes that Cu^{2+} ions are reduced immediately in a sulfuric acid medium to the elemental state, while on p. 34 it is stated that during titration of a hot sulfuric acid solution of cupric sulfate with $CrSO_4$, no deposition of metallic copper is observed right at the beginning, but cuprous sulfate is formed which subsequently disproportionates to metallic copper and $CuSO_4$. On p. 35 (23 lines from the top) while dealing with paper [95] published in 1943, the author mentions a similar paper on the determination of copper [71] published in 1938 only mentioned on 63. We do not agree that CO_2 removes Cl_2 (a heavier gas) from solution without boiling the solution (p. 71). Of interest to the reader is a technique for the determination of oxygen dissolved in water in the presence of nitrites, consequently it should be mentioned on p. 79. On p. 83 the author points out that during titration of a solution containing Se^{4+} and Cu^{2+} in a medium of 9 N HCl at 70°, in a medium of 6 N HCl at room temperature, and in a medium of 6 N H_2SO_4 at 70°, with a solution of chromous sulfate, selenium is always reduced first. On p. 84 it is stated, however, that "in a medium of 6 N H_2SO_4 at 70° there is observed simultaneous reduction of copper with quadrivalent selenium." This contradiction should be removed. There is an unfortunate expression on p. 88 (20 lines from the bottom) "a distinct potential jump of the platinum electrode was observed on completion of its reduction to the quinquevalent state." The theoretical bases of the standardization of solutions of divalent chromium salts by Stone's method are not described clearly enough.

There are many minor mistakes in the book.

All the shortcomings noted do not detract from the general good impression created by the monograph reviewed, which is undoubtedly necessary and useful. The monograph will be welcomed with great interest by its readers.

ALEKSANDR PETROVICH TERENT'EV

(On his 70th Birthday)

Commission on Analytical Chemistry
Editorial Board of Zhurnal Analiticheskoi Khimii
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 6,
pp. 747-748, November-December, 1961

Aleksandr Petrovich Terent'ev, one of the most outstanding Soviet organic chemists, a corresponding member of the Academy of Sciences, USSR, and a professor of Moscow University celebrated his seventieth birthday in 1961. A student and coworker of N. D. Zelinskii, he has taken over in full the broad scientific interests and the original teaching mastery of his teacher. A. P. Terent'ev has developed and introduced into practice a number of new synthetic methods which have found use for various classes of organic compounds.

An important feature of A. P. Terent'ev's work is the synthesis and study of the properties of organic complex compounds, and, in particular, intracomplex compounds. He has made a particularly important contribution to organic analysis.

A characteristic feature of A. P. Terent'ev's scientific achievements is his endeavour to extend the field of application of the new reactions and compounds he has studied. In this connection no less important is their use in analysis. Thus having done a considerable amount of work on the synthesis of diazo compounds, A. P. Terent'ev suggested a method for the quantitative determination of compounds with conjugated short bonds by coupling with diazotized p-nitroaniline (1936). This method possesses a high sensitivity and permits determination of conjugated dienes in the presence of a large excess of olefins.

By studying the structure and properties of magnesium organic compounds, A. P. Terent'ev basically improved the Chugaev-Zerewitinov method of determining active hydrogen. The Zerewitinov method involves a difficult measurement of the volume of methane liberated on the basis of the expansion of the gas, and in this connection it is envisaged that the reaction is carried out, not in ether, but in a high boiling solvent.

A. P. Terent'ev (1940-1947) when using the Chugaev method for the determination of active hydrogen, adopted the technique of expelling the methane liberated with ether vapor, which essentially simplified the apparatus and experimental technique, and enabled a more active ethereal solution of the magnesium organic compound to be used which cut down the time of a determination several times. Determination of active hydrogen by the Chugaev-Terent'ev method is widely used both in scientific research and for production control.

A. P. Terent'ev has suggested an original method for the analysis of oleum which is widely used in many laboratories.

In the first post-war years A. P. Terent'ev together with coworkers finished developing methods for the sulfonation of organic compounds with sulfur trioxide bound as a complex. They used this powerful synthetic method for analytical purposes for the quantitative determination of certain forms of active hydrogen. For example, by the action of a standard solution of sulfur trioxide on a hydroxyl compound an alkylsulfuric acid is formed which is then diluted with water and titrated with alkali. From the titer difference it is possible to assess the amount of sulfur trioxide which has reacted, i.e., to assess the equivalent of the hydroxyl compound. The method is distinguished by the fact that appreciable amounts of water do not interfere. Many other forms of active hydrogen and certain functional groups have been determined in a similar way.

Toward the end of the thirties A. P. Terent'ev devoted a lot of time to a study of the properties and reactions of acrylonitrile. On the basis of this work A. P. Terent'ev et al. developed a number of methods for the quantitative determination of acrylonitrile. The most interesting and effective method is the quantitative interaction of acrylonitrile with sodium sulfite in aqueous solution. During this reaction sodium hydroxide is liberated which can be titrated by any known method. Having acquired such a convenient method of determining acrylonitrile, A. P. Terent'ev with his characteristic perspicacity, has already used it for the analysis of a number of cyanoethylated compounds. An aliquot of the compound is mixed with a standard solution of acrylonitrile and the unreacted acrylonitrile back titrated after a definite time. This method has proved exceptionally convenient for the determination of thioalcohols, thiophenols, etc.

The brilliant imagination and exceptional inventiveness of A. P. Terent'ev has enriched many branches of chemical organic analysis. In the field of elemental organic analysis, he and his student, now Doctor of Science, P. N. Fedoseev have suggested methods of decomposing organic compounds with magnesium, calcium, and magnesium nitride.

In another series of papers A. P. Terent'ev and B. M. Luskina developed a new, practically valuable variant of the "wet combustion" technique which permits simultaneous determination of carbon, halogen, and nitrogen, and also metal ions and silicon in the mineralized residue.

In the field of inorganic analysis A. P. Terent'ev et al. have suggested a number of new organic reagents. A. P. Terent'ev's idea of "in situ nascendi reagents" which has been developed by a number of authors is interesting and fruitful. The ions to be precipitated and the precipitant ions are present in solution, not in a ready state, but in a bound form, the inorganic ions, in the form of unstable complex compounds, the precipitant, in the form of organic compounds. The latter on hydrolyzing liberate the necessary ions in the solution. Slow formation of precipitant and the ion to be precipitated promotes the formation of well formed crystals. For example, A. P. Terent'ev suggested the use of dimethyl sulfate in the presence of sugar for the precipitation of barium ions. Under such conditions exceptionally large and readily filtrable crystals of barium sulfate are formed. Under the same conditions, but in the presence of dioxane, calcium is precipitated as $CaSO_4 \cdot 0.5H_2O$, and in this way can be determined in the presence of appreciable amounts of strontium.

A large monograph would be necessary to catalogue the numerous and diverse researches of A. P. Terent'ev in the field of analytical chemistry, but the significance of A. P. Terent'ev's activity for Russian organic analysis could not be exhausted by any method.

A. P. Terent'ev is rightly regarded as an outstanding organic analyst. This is not simply because he has created a school of analysts, and that hundreds of his pupils are working successfully in various corners of our country. A. P. Terent'ev is an untiring propagandist of new, progressive methods of analysis, a severe critic, and an invaluable and kind consultant. On his recommendation, and under his editorship, a series of valuable analytical textbooks have been published in Russian: A. P. Terent'ev has been for many years an active member of the Commission on Analytical Chemistry and a member of the editorial board of "Zhurnal Analiticheskoi Khimii."

We should like to wish him new, important, creative successes in all his manifold scientific, social, and teaching activities.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	TRANSLATION BEGAN Issue	TRANSLATION BEGAN Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
	Life Sciences	Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
	Earth Sciences	Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106- 123	1 6	1957- 1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106- 123	1 6	1957- 1958
	Mathematics	Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
	Physics	Soviet Physics—Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106- 117	1	1956- 1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics—Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. meta'	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (In English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.